VOLUMETRIC PROPERTIES OF CORROSIVE GASES

I. The Volumetric Behavior of Nitrogen Dioxide

II. The Volumetric Behavior of Nitric Oxide

III. The Volumetric Behavior of Six Mixtures in the Binary System Nitrogen Dioxide - - Nitric Oxide

IV. The Volumetric Behavior of Four Mixtures in the Binary System Hydrogen Sulfide - Water

V. Thermodynamic Properties of Nitric Oxide

VI. Thermodynamic Properties of Nitrogen Dioxide

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ABSTRACT

Part I: The volumetric behavior of nitrogen dioxide was determined experimentally at temperatures between 100 and 340°F for pressures up to 2000 pounds per square inch. The two-phase data are compared with the results obtained by other investigators. The measurements were made in a stainless steel cell of essentially constant volume, and the experimental apparatus is described.

Part II: The volumetric behavior of nitric oxide was determined experimentally at temperatures between 40 and 220°F for pressures up to 2500 pounds per square inch. The measurements were made in a variable volume container of chrome-nickel stainless steel with mercury as the confining fluid. Reaction between the mercury and the nitric oxide was experienced at temperatures of 280°F and above.

Part III: The volumetric behavior of six mixtures in the binary system nitric oxide - nitrogen dioxide was determined in an essentially constant volume apparatus over a temperature range from 10 to 340°F. The composition range was from 0 to 20 weight percent of nitric oxide, and the maximum pressure obtained was approximately 600 pounds per square inch.

Part IV: The volumetric behavior of four mixtures in the binary system hydrogen sulfide - water was determined in an essentially constant volume apparatus over a temperature range from 10 to 340°F.

Part V: Thermodynamic properties of nitric oxide were calculated from the data presented in Part II of this thesis. Values of entropy, enthalpy, and of the ratio of fugacity to pressure are presented at temperatures of 40, 100, 160, and 220° F for pressures up to 2500 pounds per square inch.

Part VI: Thermodynamic properties of nitrogen dioxide were calculated from the data presented in Part I of this thesis. Values of entropy, enthalpy, and of the ratio of fugacity to pressure are presented for the equilibrium material, the molecular weight of which is taken as that of nitrogen dioxide, at temperatures between 160 and 340° F for pressures up to 1000 pounds per square inch.

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GENERAL INTRODUCTION

The Chemical Engineering Laboratory of the California Institute of Technology has been studying the volumetric properties of nitrogen dioxide and of mixtures of nitrogen dioxide and nitric oxide under a contract from the Office of Naval Research (1).[1] The interest in these compounds arose from the possibility of the use of nitrogen dioxide as an oxidant in liquid fuel rockets. It was thought that the addition of nitric oxide to liquid nitrogen dioxide in amounts up to the eutectic concentration would lower the freezing point of the mixture sufficiently so that it would be suitable for use in arctic regions. The studies described herein on nitrogen dioxide and nitric oxide extend to higher temperatures and pressures than have previously been reported in the literature.

It was found possible to obtain the data on nitric oxide reported in Part II of this thesis in a volumetric apparatus containing a variable volume cell with mercury as the confining fluid which was already available in the Chemical Engineering Laboratory. However, it was not practical to use mercury as the confining fluid during studies of nitrogen dioxide, previous investigations having indicated that the rate of reaction of mercury and thoroughly dehydrated nitrogen dioxide is high even at normal temperatures (2).

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[1] References are found on pages 91 and 92.

As no suitable liquid substitute for mercury as a confining fluid is available, the use of a volumetric apparatus with variable volume cell was impractical. Accordingly, an apparatus with a constant volume cell was designed and constructed. This apparatus is described in some detail in this thesis.

The American Petroleum Institute Research Project 37, which is administered by the Chemical Engineering Laboratory of the California Institute of Technology, indicated interest in the use of this latter apparatus in the study of the volumetric properties of the binary system hydrogen sulfide - water. The results of initial measurements on four mixtures in this binary system are presented in Part IV of this thesis.

DESCRIPTION OF ISOCHORIC VOLUMETRIC APPARATUS

An apparatus designed for the determination of the volumetric behavior of fairly corrosive fluids over a range of pressures from 100 to 10,000 pounds per square inch absolute and temperatures from -30 to 360°F has been constructed. This equipment may be used for any fluid which does not corrode stainless steel rapidly, and it was used for the experimental work reported in Parts I, III, and IV of this thesis. The equipment used for the measurements reported in Part II is described separately in that section. In principle, the isochoric measurements involve the determination of the equilibrium pressure for a system of constant weight and of known and nearly constant volume for each of a series of temperatures. This apparatus has previously been described and the details of calibration given (3), but a brief description of the apparatus is again included here.

Considerable experience has been had by the Department of Chemical Engineering in the past in the design and construction of variable volume apparatus to determine the volumetric behavior of gases (principally hydrocarbons). Consequently, standardized designs and techniques were available and were used where possible in the design of the present apparatus. The test chamber of this apparatus consists of a stainless steel (American Iron and Steel Institute specification number 302) sphere of approximately 5-inch inside diameter. This sphere has a minimum thickness of 0.50 inch and is composed of two threaded, hemispherical sections. The threaded portions of each hemisphere were carefully tinned with a solder containing 97 weight per cent tin and 3 weight per cent lead, and the hemispheres were joined while the solder was molten. The attainment of equilibrium is hastened by the continual oscillation (at a rate of 70 oscillations per minute) of this spherical chamber through 180°. Two valves are mounted opposite each other on the diameter of the cell normal to the axis of suspension. The three tubing connections (at present of 0.063-inch inner diameter hypodermic tubing) to the working chamber are wound in a helical spiral to enable them to flex with the oscillatory motion. The requisite quantity of each of the desired components is added to or withdrawn from the spherical container by conventional weighing bomb techniques. Figure 1 shows the agitator mechanism; and Figure 2 is a photograph of the assembled bomb, the diaphragm mechanism discussed below not being in place.

The pressure within the equilibrium chamber is determined by means of a pressure balance already mounted and in use in the Chemical Engineering Laboratory. This pressure balance is periodically calibrated against the vapor pressure of carbon dioxide at the ice point. A stainless steel diaphragm of 0.010 inch in thickness is used to separate the material being tested from the silicone in the adjacent portion of the hydraulic system. The pressure is balanced by use of an electrical contact which completes a circuit with the diaphragm from the motion of the diaphragm produced by a pressure in the working section of approximately 1.0 pound per square inch greater than that in the hydraulic system. Because the pressure balance used operates with oil as the hydraulic fluid, a trap consisting of a mercury-in-steel U-tube is used to seperate the oil and silicone portions of the hydraulic system. An electrical contact in each side of the trap permits the location of the mercury interfaces to be determined and reproduced. Displacement cylinders of a design which is standard in the laboratory are used to maintain proper amounts of oil and silicone in the separate parts of the hydraulic system. Figure 3 consists of photographs of an assembled and disassembled displacement cylinder. Silicone rather than oil is used in the portion of the hydraulic system adjacent to the diaphragm in order to eliminate any possibility of decomposition of the hydraulic fluid at higher temperatures.

The temperature of the spherical working section is controlled by immersing it in an agitated liquid silicone bath. Figure 4 is a photograph of the impeller mechanism. Silicone is used because of its relatively small change in viscosity with change in temperature. If oil were used in the fluid bath, several changes of oil would have to be made during each series of measurements, if the equipment were to operate over the proposed temperature range. The temperature of the sample is determined by measuring the temperature of the bath at equilibrium, using a strain-free platinum resistance thermometer. A second strain-free platinum resistance thermometer is connected to a droop-corrected Thyratron control circuit (4) which can maintain the temperature at any desired value in the operating region.

The above-mentioned bath is surrounded by a dead-air space approximately one inch in width and then by a steel radiation shield. Two inches of magnesia insulation then surround the radiation shield. Figure 5 is a photograph of the top view of the bath with the top of the radiation shield removed. The spherical cell is shown mounted in position. A 1000-watt, switch-operated (non-variable voltage supply) heater is wrapped around the bath. There are six separate heating circuits wound on the radiation shield beneath the magnesia insulation. Two of these heating circuits are 500-watt, switch-operated heaters. The other four circuits, also each of 500 watt capacity, have their inputs controlled by Variacs and are mounted one each on the top, bottom, upper half, and lower half of the radiation shield. Four sets of differential thermocouples between appropriate areas on the bath and the shield are used for precise adjustment of the Variacs. Each of the shafts which penetrate the radiation shield (the shaft of the bath impeller, the shaft of the bomb agitator, and the silicone overflow pipe) is designed to have a 100-watt heater wound on, with the input controlled by a

Variac. Thus calorimetric techniques are used throughout. When the bath is at a controlled temperature, only the heaters on the radiation shield plus the heater connected to the electronic control circuit (a 500-watt heater suspended in the bath) are in use. The switch-operated heating elements are used only to facilitate rapid changes from one control temperature to the next. Figure 6 is a photograph of the electrical panel of the test apparatus and photographs of the associated temperature bench. The temperature bench, at which all electrical measurements are made, is of a design standard in the laboratory.

The refrigeration facilities are designed so that the temperature of the test section of the apparatus can be reduced from 400 to 0°F in approximately 1.5 hours and so that a minimum temperature of at least -25°F can be attained. A three-ton rated capacity Freon refrigeration unit was available in the laboratory and was used as the basic refrigeration source. However, Freon could not be used directly as the refrigerant because of decomposition of both Freon and of the lubricating oil circulated in the Freon system. Thus the identical silicone liquid used in the hydraulic and temperature control systems was also chosen as the cooling medium for the same reasons of stability and relatively small change in viscosity with temperature mentioned previously, and a Freon-silicone heat exchanger was designed. Two independent silicone cooling systems are used, one containing refrigerating coils soldered to the silicone bath, and the other containing coils soldered to the radiation shield beneath the magnesia insulation. The bath refrigeration system is used only to speed the rate of cooling, and it is shut off once a desired low temperature is reached. The radiation shield refrigeration system is used to balance heat gains from the surroundings. Each silicone refrigeration system is operated by a gear pump and contains a standpipe on the low pressure side of the pump to allow for expansion of the silicone, a valve-controlled by-pass around the pump, and a pressure gauge on the high pressure side. The silicone from the high pressure side of the pump flows through the freon heat exchanger before entering the refrigeration coils. Figures 7 and 8 are photographs which show the appearance of parts of the refrigeration system.

The equipment, excluding the instruments required for the measurement and control of temperature which are in the associated temperature bench, is housed in a steel and aluminum structure approximately 7 feet square and 6 feet high. In order to protect the operator, that portion of the structure containing the working section and silicone bath is surrounded on all sides save the top by a hot-rolled steel plate 0.5 inch in thickness.

Figure I: Agitator Mechanism

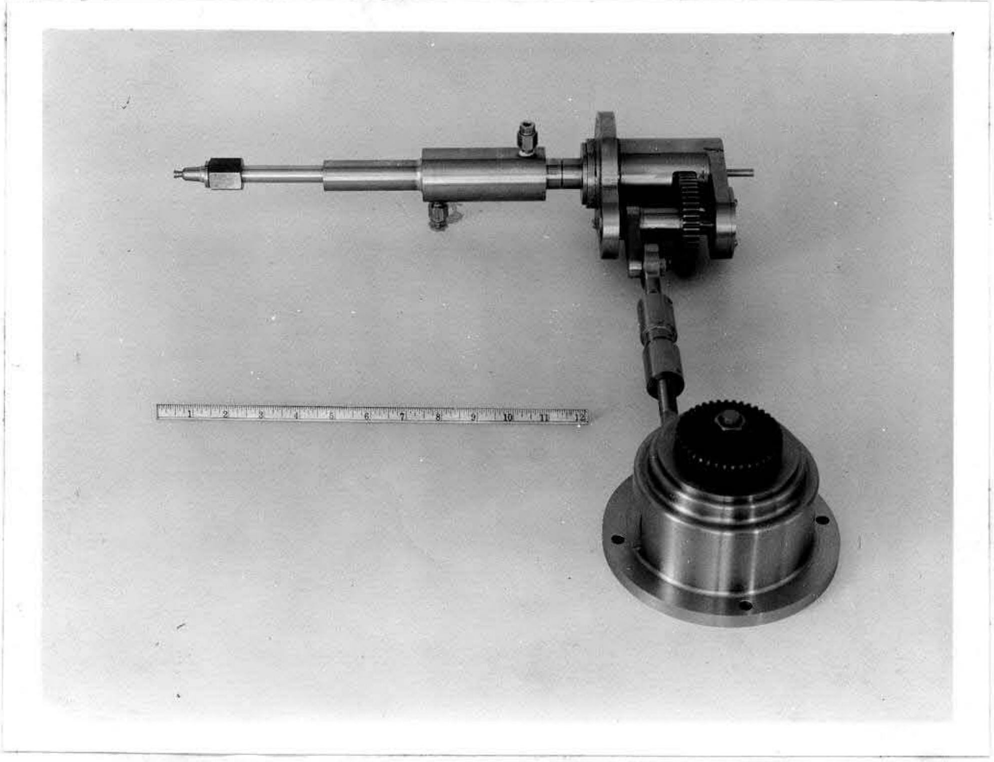


Figure 2: Assembled Bomb, Diaphragm Assembly not in Place

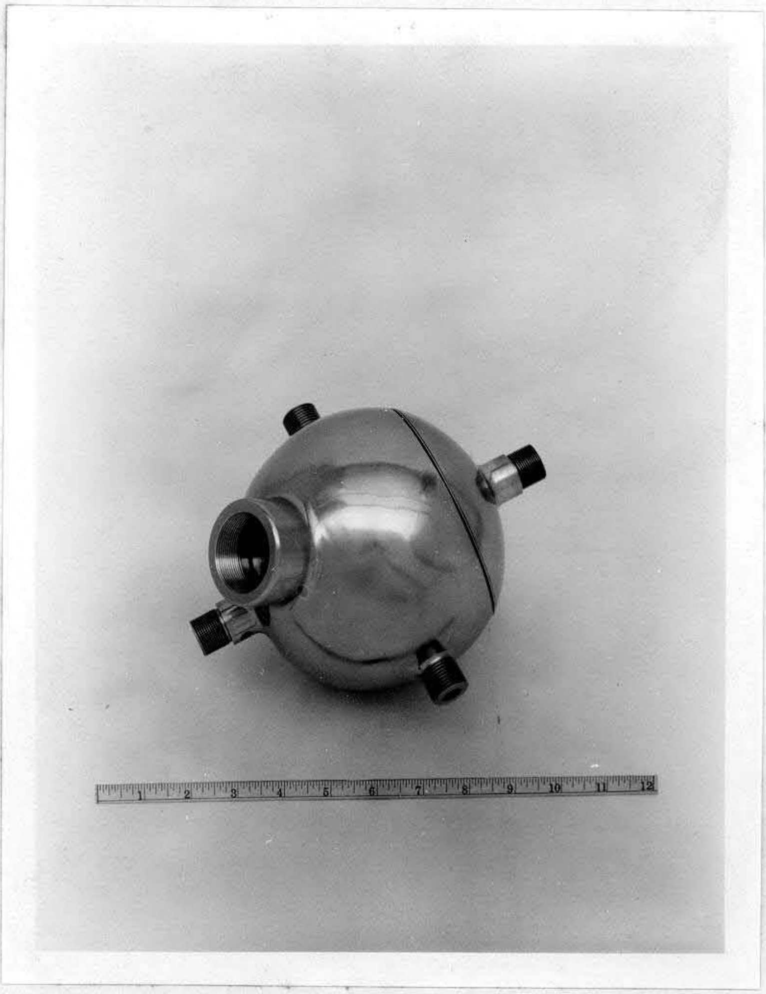
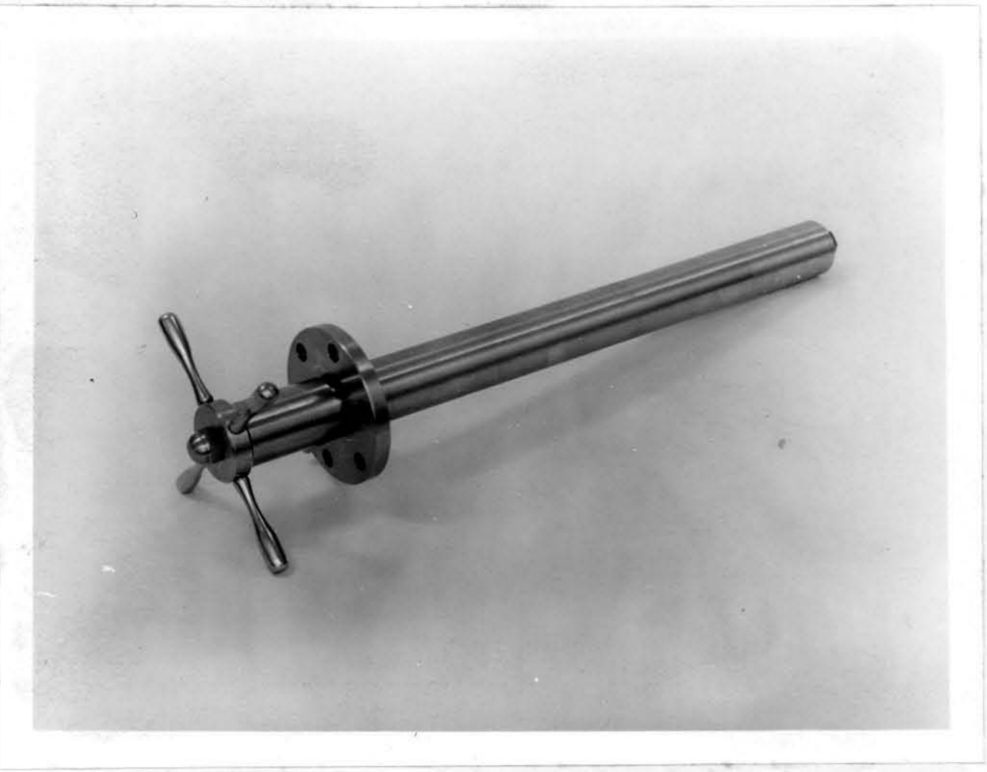
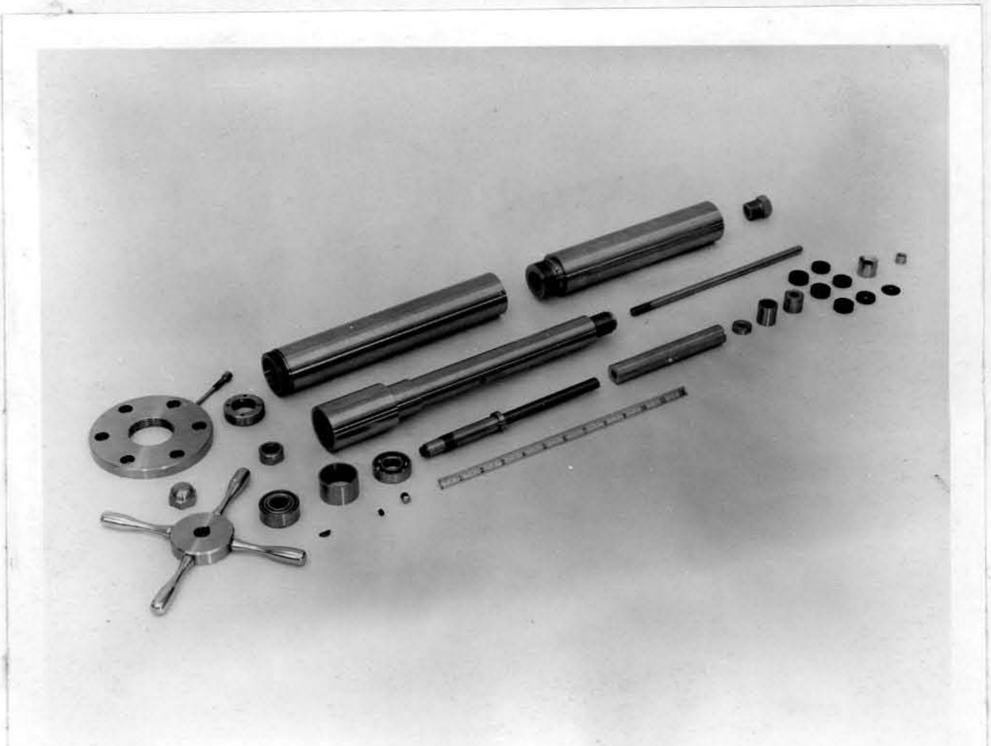


Figure 3: Assembled and Disassembled Views of Displacement Cylinder



Assembled Displacement Cylinder



Disassembled Displacement Cylinder

Figure 4: Impeller Mechanism

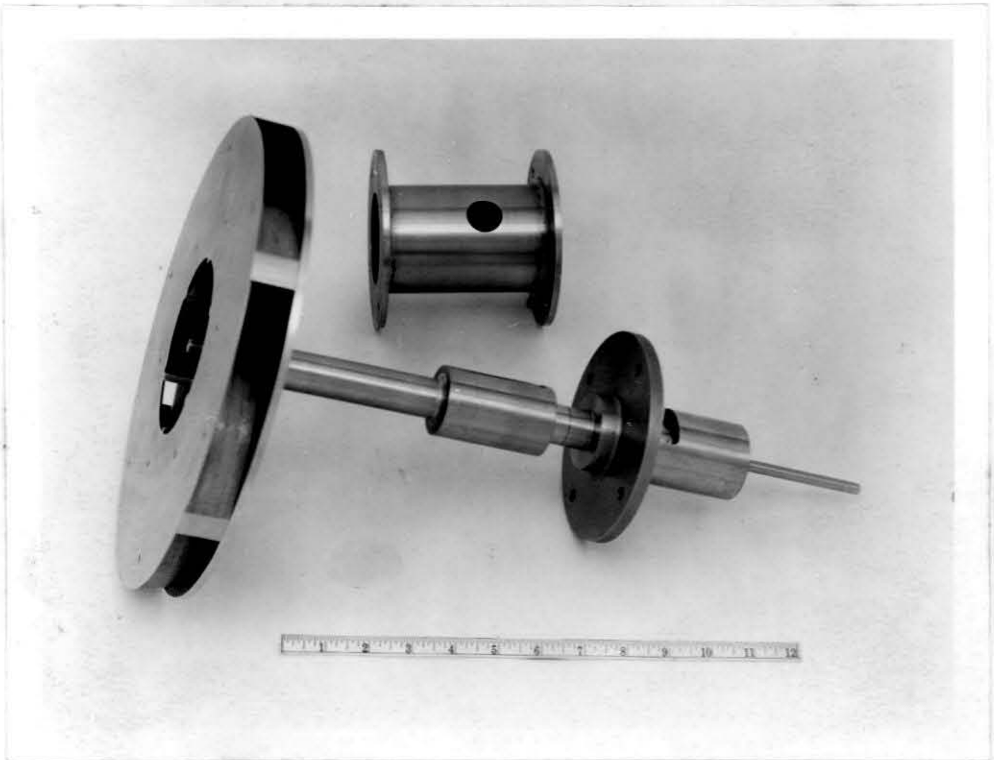


Figure 5: Top View of Bath with Top of Radiation Shield Removed. This Photograph shows Bomb Mounted in Position

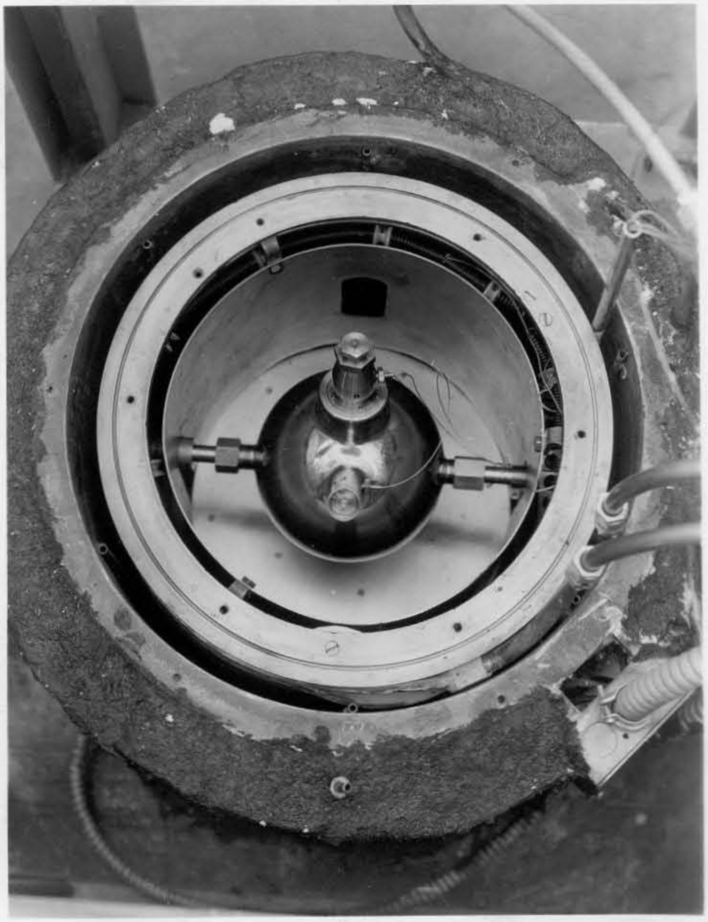
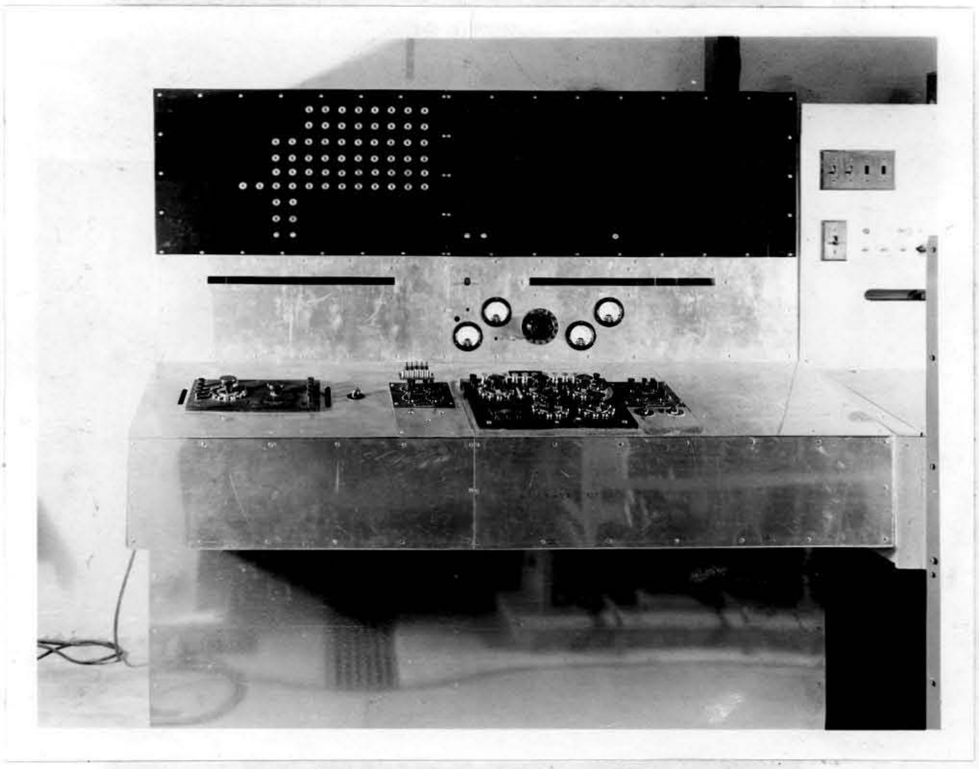


Figure 6: Views of Temperature Bench and Electrical Panel of Volumetric Apparatus

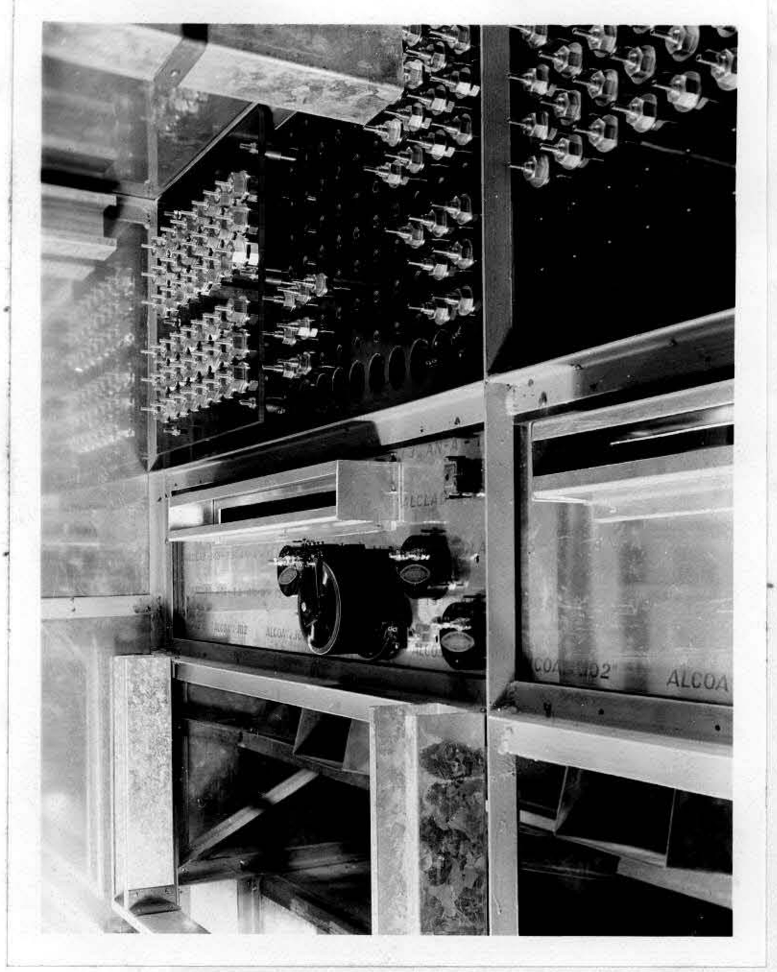
a) Electrical Panel of Volumetric Apparatus (Shown in Process of Construction) showing Location of Temperature Bench

Figure 6: (Continued)



b) Front View of Temperature Bench

Figure 6: (Continued)



c) Interior Layout of Temperature Bench

Figure 7: Valve Panel of Volumetric Apparatus. This photograph shows displacement cylinders mounted. It also shows the radiation shield in position with its associated power and refrigeration lines.

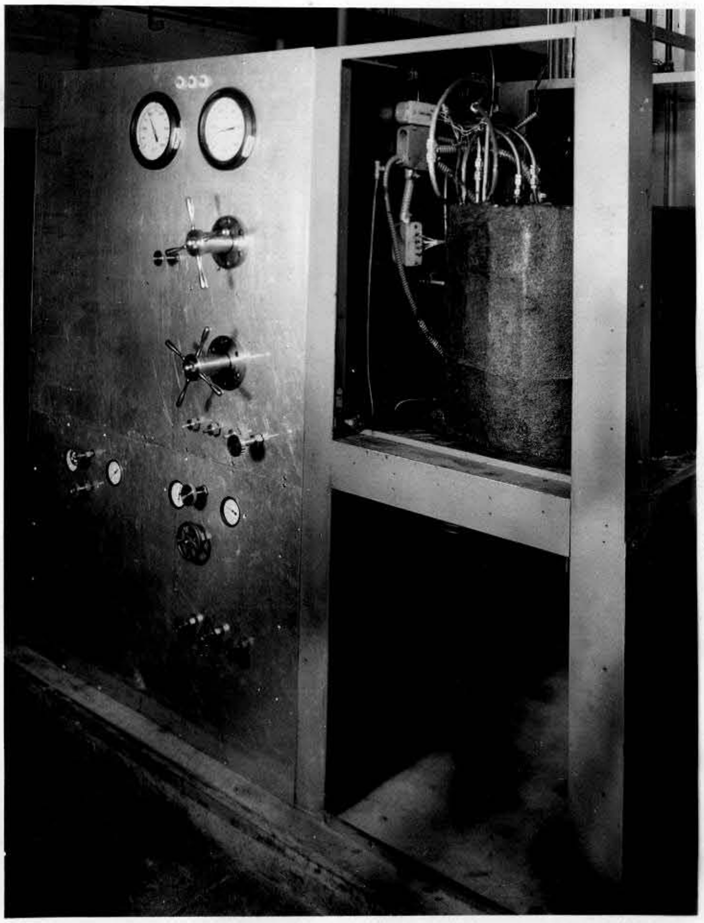
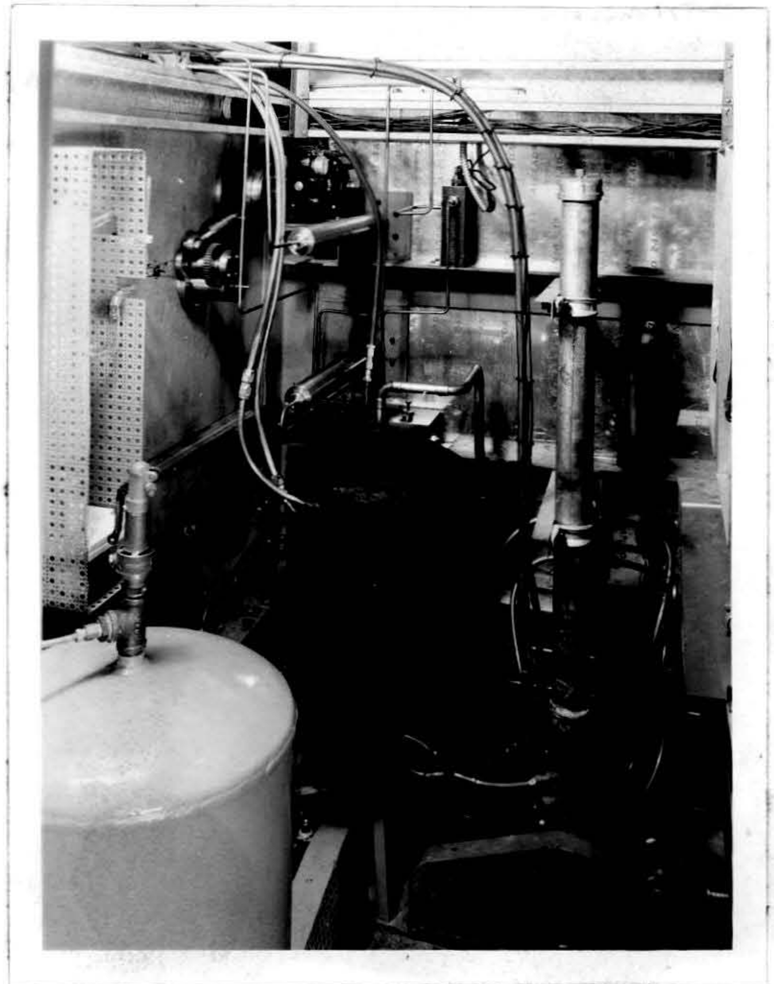


Figure 8: Interior of Volumetric Apparatus Housing. The agitator mechanism and displacement cylinders are shown mounted. The freon-silicone heat exchanger is shown as are the silicone flow lines.



PART I

THE VOLUMETRIC BEHAVIOR OF NITROGEN DIOXIDE

INTRODUCTION TO PART I

A large amount of research has been done on the properties of the oxides of nitrogen because of the formation of these gases in the major industrial methods for the manufacture of nitric acid. The physical constants of NO_2 and N_2O_4 have been determined with great care (5). The equilibrium constant of the rapid, reversible reaction $N_2O_4 \rightleftharpoons 2\ NO_2$ has been determined over various temperature ranges by several investigators (6). The equilibrium constant (5) and reaction rate (7,6) of the moderately slow, reversible reaction $NO_2 \rightleftharpoons NO + \frac{1}{2}\ O_2$ have also been determined, only little decomposition being found at normal temperatures. Moreover, the vapor pressure of nitrogen dioxide was measured by Scheffer and Treub (8), Baume (9), and Mittasch (10), although only the studies of Scheffer and Treub were carried to temperatures above 130°F.

The measurements reported in this thesis are, of course, concerned in all cases with the equilibrium mixture of NO_2 and N_2O_4 present under the specified conditions.

MATERIALS

The nitrogen dioxide used in the present measurements was obtained from the Allied Chemical and Dye Corporation. It was purified by fractionation at atmospheric pressure in a glass column provided with sixteen plates at a reflux ratio of eight. The first one-fifth of the distillate was discarded, and the central fraction, which boiled in a temperature range of less than 0.1°F was retained. This central fraction was passed over phosphorus pentoxide at approximately one atmosphere pressure and condensed in a glass capsule at a pressure below 0.1 millimeter of mercury. The condensing agent was a bath of solid carbon dioxide and acetone. The nitrogen dioxide thus purified was stored in stainless steel containers until used.

EXPERIMENTAL MEASUREMENTS

Twelve samples of nitrogen dioxide were used in the experimental measurements. These measurements involved the determination of pressure as a function of temperature for each constant weight of sample confined in the working cell. The studies involved a range of specific volumes from 0.03386 to 2.464 cubic feet per pound. Each sample was investigated in the temperature range from 100 to 340°F at temperature intervals of 30°F, including pressures up to 2000 pounds per square inch absolute.

Measurements of the vapor pressure of nitrogen dioxide were made. The experimental results are recorded in Table I, which gives corresponding values of temperature, pressure, and two-phase specific volume. Smoothed values of the vapor pressure are recorded for even values of the temperature in Table II. Figure 9 presents the results of these vapor pressure measurements as plotted on a residual basis. The relationship between the reference vapor pressure P_r'', the actual vapor pressure P'', and the residual vapor pressure $\underset{\sim}{P}''$ is:

$$P'' = P_r'' - \underset{\sim}{P}''$$

where the reference vapor pressure P_r'' is specified by the following expression:

$$\log_{10} P_r'' = 7.57156 - 3423.98/T$$

The experimental values of Scheffer and Treub and of Mittasch are also included in Figure 9 for purposes of comparison.

The results of the experimental measurements obtained in the one-phase region with these twelve samples are presented in Figure 10, which outlines the volumetric behavior of nitrogen dioxide in the region specified. The average values of specific volume indicated in this figure were obtained by considering an average total volume of the cell in the range of temperatures and pressures encountered in the one-phase region in each case. This variation in the total volume of the cell introduces a maximum error in the indicated specific volumes of less than 0.3 per cent. The tabulated data and other figures do not incorporate this approximation, which is used in Figure 10 only so that the isochoric variation of pressure with temperature may be shown conveniently.

The behavior of the compressibility factor is shown in Figure 11. The compressibility factor Z is defined as follows:

$$Z = PVM/RT$$

in which M, the molecular weight of nitrogen dioxide, is taken as 46.008. Figure 12 shows the behavior in the low-pressure region on a relatively large scale, and includes the experimental data of Verhoek and Daniels (6) and of Mittasch.

The experimental values of pressure and specific volume are recorded in Table III for even values of temperature in the single-phase region. Table IV contains smoothed values of compressibility factor and specific volume for even values of temperature and pressure.

The molecular weight of the dew-point gas appears to approach 92.016 as the pressure is reduced towards zero. The effects of pressure and temperature upon the reversible reaction

$$N_2O_4 \rightleftharpoons 2\ NO_2$$

are indicated by the somewhat unusual behavior of the isotherms and the dew-point curve in Figure 11. It is believed that the data presented in this thesis describe the behavior of nitrogen dioxide at chemical as well as at physical equilibrium. Constancy of pressure was attained at each state recorded and this pressure was reproducible upon approach from either lower or higher pressures. Reaction rate measurements upon the reversible reaction

$$NO_2 \rightleftharpoons NO + \tfrac{1}{2}\ O_2$$

which is of importance at the higher temperatures encountered in the present studies were previously noted. These measurements also indicate that equilibrium at each state should be closely approached under the conditions of the present study within the time required to obtain the data at that state (11).

It is believed that the temperatures of measurement were known within 0.03°F relative to the international platinum scale and the pressures within 0.1 pound per square inch or 0.1 per cent, whichever is larger. The nitrogen dioxide was introduced into the apparatus by use of a weighing bomb with a probable uncertainty in the introduced weight of less than 0.1 per cent.

TABLE I.

Experimental Values of Vapor Pressure of Nitrogen Dioxide

Temperature, °F.	Pressure Lb./Sq.Inch Absolute	Specific Volume, Cu. Ft./Lb.
100	30.74	0.38909
	30.45	0.26257
	30.67	0.063699
130	60.01	0.063751
160	111.39	0.38972
	111.15	0.17228
	111.56	0.13840
	111.27	0.063803
190	196.36	0.063855
220	331.57	0.079563
	332.55	0.063908
	332.98	0.13863
250	543.93	0.063963
280	864.08	0.064018
290	1002.5	0.064045
300	1158.0	0.064056
	1160.1	0.033859

TABLE II

Vapor Pressure of Nitrogen Dioxide

Temperature, ° F.	Pressure, Lb./Sq.Inch Absolute	Temperature, ° F.	Pressure, Lb./Sq.Inch Absolute
70	14.78	200	235.01
80	18.98	210	281.56
90	24.21	220	332.8
100	30.69	230	393.2
110	38.62	240	463.3
120	48.24	250	543.9
130	59.98	260	636.3
140	74.12	270	732.6
150	91.06	280	864.1
160	111.24	290	1002.5
170	135.14	300	1160.1
180	163.29	310	1336.5[a]
190	196.35	316.8	1469.0[a,b]

[a] Value extrapolated.

[b] Critical pressure estimated from measuredcritical temperature (10).

TABLE III.

Experimental Measurements

Pressure, Lb./Sq.Inch Absolute	Specific Volume, Cu.Ft./Lb.	Pressure, Lb./Sq.Inch Absolute	Specific Volume, Cu.Ft./Lb.	Pressure, Lb./Sq.Inch Absolute	Specific Volume Cu.Ft./Lb.
130° F.		160° F.		190° F.	
35.88	2.4578	42.09	2.4598	48.96	2.4618
220° F.		250° F.		280° F.	
55.49	2.4638	61.38	2.4658	66.40	2.4677
159.95	0.7264	182.14	0.7270	202.98	0.7276
261.32	0.3904	403.71	0.2637	344.31	0.3910
-	-	444.16	0.23095	466.67	0.2639
-	-	-	-	515.63	0.23114
-	-	-	-	631.00	0.17286
-	-	-	-	704.62	0.14543
-	-	-	-	724.13	0.13886
-	-	-	-	841.67	0.10459
310° F.		320° F.		340° F.	
70.84	2.4697	396.0	0.3914	74.73	2.4717
221.64	0.7282	760.4	0.17303	238.22	0.7288
529.0	0.2641	1362.5	0.06409	419.3	0.3916
586.6	0.23133	1550.2	0.03385	589.6	0.2643
823.2	0.14555			654.0	0.23152
848.5	0.13898	-	-	823.3	0.17314
1011.2	0.10467	-	-	939.9	0.14567
1263.5	0.06408	-	-	971.4	0.13909
1350.5	0.03384	-	-	1181.6	0.10476
-	-	-	-	1561.6	0.06413
-	-	-	-	1940.6	0.03387

TABLE IV

Volumetric Behavior of Nitrogen Dioxide

Pressure, Lb./Sq.Inch Absolute	70° F.		100° F.		130° F.		160° F.		190° F.	
	Compressibility Factor	Specific Volume, Cu.Ft./Lb.	Compressibility Factor	Specific Volume, Cu.Ft./Lb.	Compressibility Factor	Specific Volume, Cu.Ft./Lb.	Compressibility Factor	Specific Volume, Cu.Ft./Lb.	Compressibility Factor	Specific Volume, Cu.Ft./Lb.
	(14.78)[a]		(30.69)		(59.98)		(111.24)		(196.35)	
Dew point	0.5643	4.557	0.5924	2.522	0.5967	1.368	0.5957	0.7736	0.5898	0.4552
14.696	0.5662	4.760	0.6404	5.689	0.7276	6.810	0.8296	8.157	0.9129	9.414
20			0.6202	4.048	0.6984	4.803	0.7999	5.779	0.8887	6.734
30			0.5939	2.584	0.6586	3.020	0.7552	3.638	0.8510	4.299
40					0.6318	2.173	0.7217	2.607	0.8211	3.111
50					0.6120	1.684	0.6949	2.008	0.7923	2.401
60					0.5968	1.368	0.6729	1.620	0.7673	1.938
80							0.6371	1.151	0.7249	1.373
100							0.6089	0.8799	0.6928	1.050
125									0.6599	0.8001
150									0.6317	0.6382

TABLE IV (Cont.)

Pressure, Lb./Sq.Inch Absolute	220° F. Compress-ibility Factor	220° F. Specific Volume, Cu.Ft./Lb.	250° F. Compress-ibility Factor	250° F. Specific Volume, Cu.Ft./Lb.	280° F. Compress-ibility Factor	280° F. Specific Volume, Cu.Ft./Lb.	310° F. Compress-ibility Factor	310° F. Specific Volume, Cu.Ft./Lb.	340° F. Compress-ibility Factor	340° F. Specific Volume, Cu.Ft./Lb.
	(332.83)		(543.93)		(864.14)		(1336.5)			
Dew point	0.5755	0.2744	0.5465	1.663	0.4899	0.09782	0.3675[b]	0.05232[b]		
14.696	0.9567	10.321	0.9784	11.021	0.9885	11.606	0.9929	12.130	0.9956	12.637
20	0.9422	7.469	0.9711	8.038	0.9848	8.496	0.9902	8.889	0.9941	9.272
30	0.9169	4.846	0.9569	5.280	0.9771	5.620	0.9853	5.897	0.9912	6.163
40	0.8936	3.542	0.9430	3.903	0.9699	4.184	0.9804	4.401	0.9881	4.608
50	0.8725	2.767	0.9293	3.077	0.9620	3.313	0.9758	3.504	0.9852	3.676
60	0.8546	2.258	0.9165	2.529	0.9542	2.744	0.9709	2.905	0.9823	3.054
80	0.8238	1.633	0.8922	1.846	0.9393	2.026	0.9617	2.158	0.9764	2.277
100	0.7972	1.264	0.8706	1.441	0.9249	1.596	0.9523	1.710	0.9708	1.811
125	0.7684	0.9746	0.8464	1.121	0.9072	1.252	0.9409	1.351	0.9631	1.437
150	0.7425	0.7848	0.8246	0.9100	0.8898	1.024	0.9298	1.113	0.9559	1.189
200	0.6959	0.5516	0.7869	0.6513	0.8573	0.7396	0.9081	0.8152	0.9413	0.8780
250	0.6528	0.4140	0.7495 (7549)	0.4999	0.8310 (8281)	0.5735	0.8876	0.6374	0.9259	0.6909
300	0.6078	0.3212	0.7110	0.3923	0.8005	0.4604	0.8680	0.5195	0.9138	0.5682
400			0.6475	0.2680	0.7465	0.3220	0.8279	0.3716	0.8855	0.4130
500			0.5815	0.1925	0.6965	0.2403	0.7885	0.2831	0.8575	0.3199
600					0.6475	0.1862	0.7515	0.2249	0.8295	0.2568
800					0.5400	0.1165	0.6755	0.1516	0.7733	0.1803
1000							0.5935	0.1066	0.7155	0.1335
1250							0.4615	0.06627	0.6405	0.09656
1500									0.5595	0.06958
1750									0.4600	0.04903
2000									0.3065	0.02859

[a] Values in parentheses are vapor pressures expressed in pounds per square inch.

[b] These values are estimated.

Figure 9: Residual Vapor Pressure of Nitrogen Dioxide

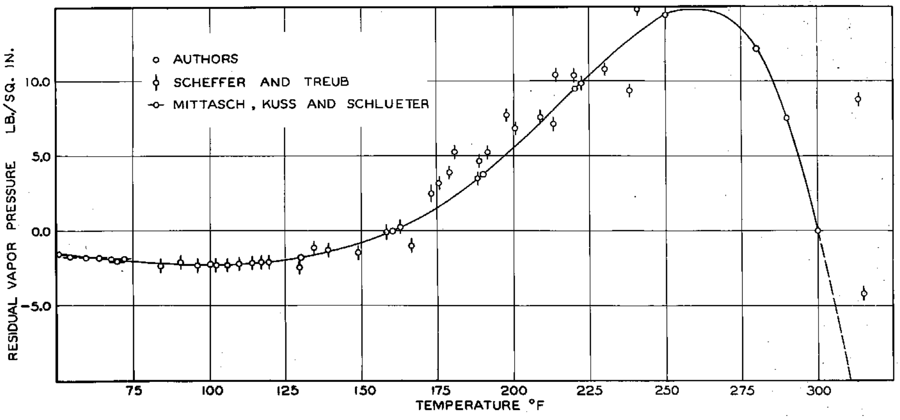


Figure 10: Pressure-Temperature Diagram for Nitrogen Dioxide

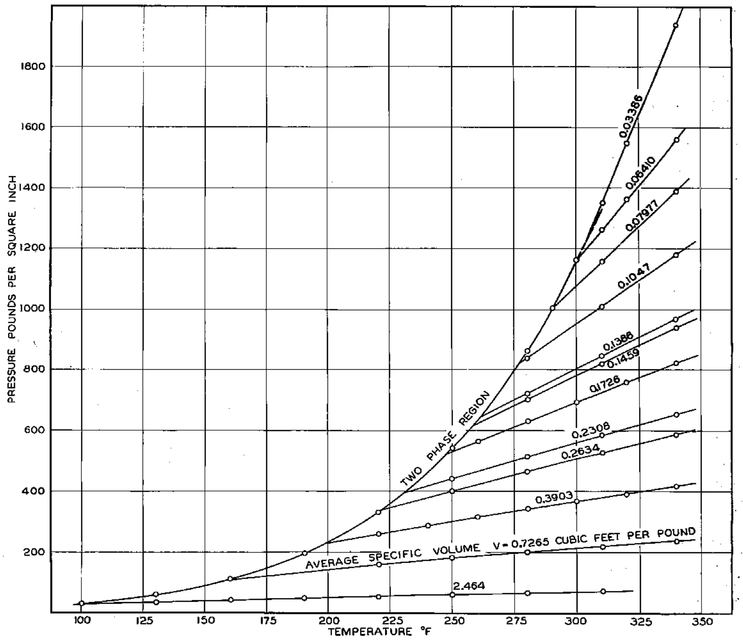


Figure 11: Compressibility Factor of Nitrogen Dioxide

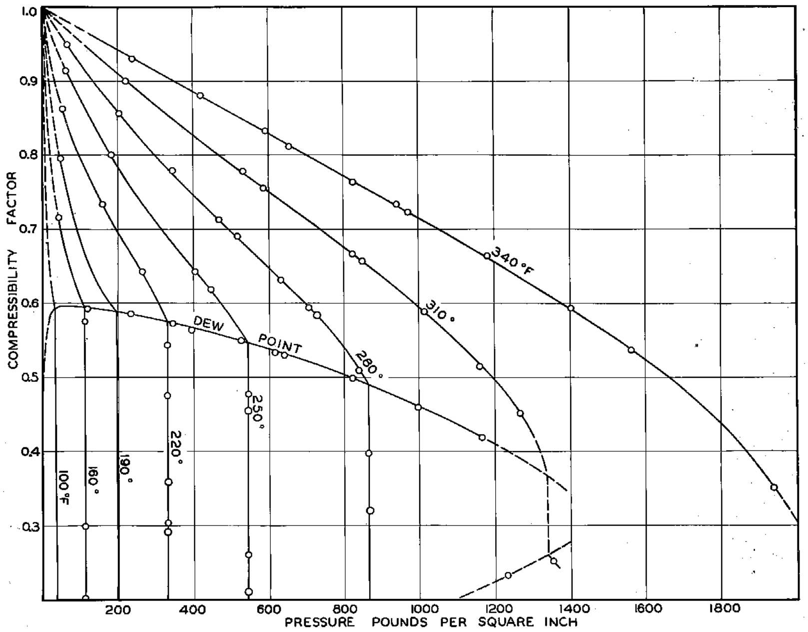
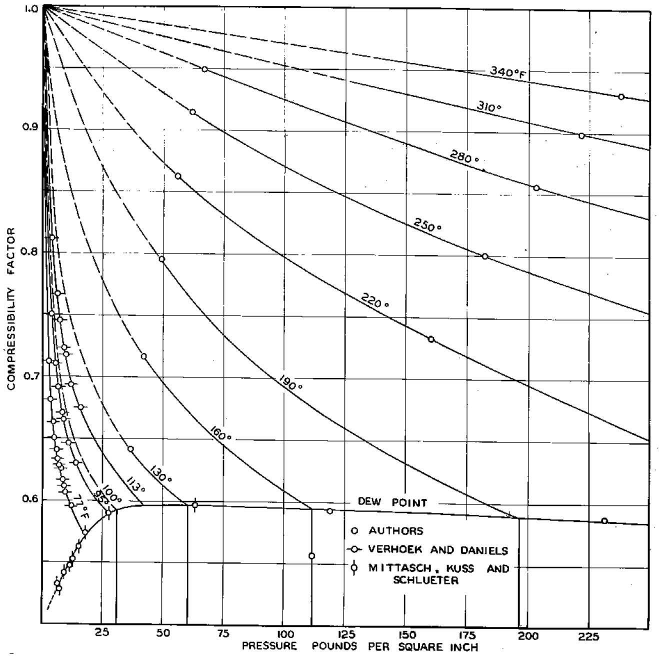


Figure 12: Compressibility Factor of Nitrogen Dioxide at Low Pressures



PART II

THE VOLUMETRIC BEHAVIOR OF NITRIC OXIDE

INTRODUCTION TO PART II

The present data in the literature upon nitric oxide are not sufficient to establish the volumetric behavior of this compound under many of the conditions encountered in industrial practice. Measurements were made of the influence of pressure and temperature upon the specific volume of nitric oxide at temperatures from 40 to 220°F at pressures up to 2500 pounds per square inch. Efforts to carry out measurements at higher temperatures resulted in significant reaction of the nitric oxide with the mercury employed as a confining agent.

Briner and coworkers (12) determined the compressibility factor of nitric oxide at five temperatures from about -109 to 48°F for pressures up to 2400 pounds per square inch. Batuecas (13) determined the average value of the compressibility factor at the ice point for pressures slightly greater than one atmosphere. The second virial coefficient was determined by Johnston and Weimar (14) as a function of temperature for temperatures from -243 to 70°F and pressures ranging from approximately one-fourth atmosphere to one atmosphere. The heat capacity, vapor pressure, and enthalpy change upon vaporization of nitric oxide were determined by Johnston and Giauque (15) for temperatures below the normal boiling point.

APPARATUS AND METHODS

The variable volume apparatus utilized in this study has been described in considerable detail (16). It involved in principle a stainless steel chamber whose effective volume could be varied by the introduction or withdrawal of mercury. This chamber was immersed in an agitated oil bath, the temperature of which was controlled within 0.03°F of the desired value. The temperature was measured by means of a strain-free platinum resistance thermometer and a Mueller type resistance bridge. The pressure was determined by use of a piston-cylinder combination incorporated in a balance system, as described earlier in connection with this apparatus (16). The balance system was calibrated against the vapor pressure of carbon dioxide at the ice point (17). It is believed that the temperatures of measurement were known within 0.03°F relative to the international platinum scale and the pressures within 0.1 pound per square inch or 0.1 per cent, whichever is larger. The nitric oxide was introduced into the apparatus by conventional weighing bomb techniques with a probable uncertainty in the weight introduced of less than 0.1 per cent (16).

After introduction of the nitric oxide, the pressure within the equipment was raised to the desired upper value by injecting mercury. The oil bath was maintained at a predetermined temperature throughout a set of measurements.

After equilibrium had been attained, as indicated by the constancy of pressure with respect to time, the total volume occupied by the nitric oxide was determined. The pressure was then decreased somewhat and the process repeated. From these measurements a set of corresponding equilibrium values of pressure and total volume were obtained for each of the temperatures at which data were taken.

MATERIAL

The nitric oxide employed in this investigation was prepared by the reaction of sodium nitrite, ferrous sulfate, and sulfuric acid in aqueous solution. The reaction, which has been discussed by Chretien and Longi (18) and others (19), proceeds as follows:

$$2\ NaNO_2 + 2\ FeSO_4 + 3\ H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2\ NaHSO_4 + 2\ HOH + 2\ NO$$

The nitric oxide was purified by use of a procedure based upon that of Johnston and Giauque (15). Two reaction solutions were used, the first an aqueous solution 1.0 M in $FeSO_4$ and 1.5 M in H_2SO_4 and the second an aqueous solution 5.0 M in $Na\ NO_2$. The solutions were prepared from J. T. Baker Company C. P. $FeSO_4 \cdot 7HOH$ and $NaNO_2$, respectively. A vacuum pump was used to de-aerate both solutions thoroughly before use. The solutions were combined under an atmosphere of nitric oxide. The nitric oxide, at a pressure of approximately one atmosphere, was passed through a trap surrounded by acetone and solid carbon dioxide and through a tube containing phosphorus pentoxide suspended on glass wool. The resulting gas was throttled to a pressure of approximately five millimeters of mercury and collected in a trap surrounded by liquid air, approximately the first one-fifth of the material thus collected was sublimed under vacuum, the central portion of the sublimate being collected in glass at the temperature of liquid air and then stored at elevated pressure in a steel vessel.

EXPERIMENTAL MEASUREMENTS

The influence of pressure and temperature upon the specific volume of nitric oxide was investigated at temperatures from 40 to 220°F, including four isotherms, and at pressures up to 2500 pounds per square inch absolute. Two different samples of nitric oxide were employed, and the results obtained from them differed from one another in the average by less than 0.05 per cent.

At temperatures of 280°F and above, marked changes in the volumetric behavior of the sample with time were experienced. These changes apparently resulted from a reaction of the nitric oxide with mercury. Examination of the cell at the completion of a set of measurements which were carried out at temperatures up to 340°F revealed the presence of an appreciable amount of mercuric oxide. No significant change in the behavior of the sample with time was noted for temperatures below 280°F. The checks on the reproducibility of the data included repeating the lower temperature isotherms after measurements had been made at the maximum temperature of 220°F. Accordingly, it is believed that the results obtained in this study do not involve significant uncertainties as a result of the reaction of nitric oxide with either mercury or stainless steel.

The compressibility factor is shown in Figure 13 as a function of pressure for each of the four temperatures investigated. The compressibility factor, Z, is defined on page 23. The experimental points shown in Figure 13 were taken from both sets of measurements on nitric oxide, as indicated. Figure 14 shows the behavior of the residual specific volume of nitric oxide as a function of temperature for a pressure of 14.696 pounds per square inch absolute. The residual specific volume, $\underset{\sim}{V}$, is defined as follows:

$$\underset{\sim}{V} = (1-Z)RT/MP$$

Although all the experimental measurements shown in Figure 13 were obtained at pressures above 170 pounds per square inch, it is possible to make accurate interpolations of the residual specific volume at lower pressures through the assumption that the residual specific volume approaches a constant value as the pressure approaches zero, and this was the procedure followed in the construction of Figure 14.

Figure 14 also presents a comparison of the data of Johnston and Weimar (14) with the present results. The agreement is within 0.0015 cu. ft/lb at temperatures up to 100°F, corresponding to agreement in specific volume within 0.1 per cent. It should again be noted, however, that the date of Johnston and Weimar result from direct experimental measurements while the values indicated in Figure 14 for the present data were obtained by interpolation of the experimental data. The equation given by Johnston and Weimar, which presented the second virial coefficient as a function of temperature, was extrapolated to temperatures above 100°F in

Figure 14.

Table V presents values of the compressibility factor of nitric oxide for even values of pressure and temperature. These results were obtained by appropriate interpolation of the experimental data presented in Figure 13. As a result of the good agreement of the two sets of experimental measurements and the care with which the samples of nitric oxide were prepared it is believed that the probable error of the values recorded in Table V is less than 0.2 per cent.

Table I. Volumetric Behavior of Nitric Oxide

	40° F.		100° F.		160° F.		220° F.	
Pressure, Lb./Sq.Inch Absolute	Compress-ibility Factor	Specific Volume Cu.Ft./Lb.	Compress-ibility Factor	Specific Volume Cu.Ft./Lb.	Compress-ibility Factor	Specific Volume Cu.Ft./Lb.	Compress-ibility Factor	Specific Volume Cu.Ft./Lb.
0	1.0000	-	1.0000	-	1.0000	-	1.0000	-
14.696	0.9990	12.15	0.9994	13.61	0.9996	15.07	0.9997	16.53
20	0.9987	8.92	0.9991	10.00	0.9994	11.07	0.9996	12.15
30	0.9981	5.95	0.9986	6.66	0.9992	7.38	0.9995	8.10
40	0.9973	4.46	0.9981	4.99	0.9989	5.53	0.9994	6.07
50	0.9967	3.56	0.9976	3.99	0.9986	4.43	0.9993	4.86
60	0.9959	2.966	0.9971	3.33	0.9983	3.69	0.9991	4.05
80	0.9945	2.221	0.9961	2.492	0.9978	2.764	0.9987	3.03
100	0.9929	1.774	0.9951	1.992	0.9972	2.210	0.9984	2.427
125	0.9909	1.416	0.9938	1.591	0.9965	1.767	0.9979	1.940
150	0.9889	1.178	0.9926	1.324	0.9958	1.471	0.9975	1.616
200	0.9849	0.8800	0.9902	0.9909	0.9945	1.102	0.9968	1.211
300	0.9768	0.5818	0.9856	0.6576	0.9919	0.7327	0.9954	0.8065
400	0.9691	0.4329	0.9813	0.4910	0.9894	0.5481	0.9942	0.6041
500	0.9618	0.3437	0.9773	0.3912	0.9870	0.4375	0.9933	0.4829
600	0.9550	0.2844	0.9737	0.3248	0.9847	0.3637	0.9925	0.4021
800	0.9424	0.2105	0.9671	0.2420	0.9808	0.2717	0.9915	0.3012
1000	0.9309	0.1663	0.9613	0.1924	0.9780	0.2167	0.9912	0.2409
1250	0.9169	0.1311	0.9559	0.1531	0.9760	0.1730	0.9913	0.1928
1500	0.9036	0.1076	0.9516	0.1270	0.9750	0.1440	0.9915	0.1607
1750	0.8921	0.09109	0.9485	0.1085	0.9746	0.1234	0.9926	0.1379
2000	0.8831	0.07890	0.9465	0.09472	0.9749	0.1080	0.9947	0.1209
2250	0.8755	0.06953	0.9454	0.08410	0.9759	0.09612	0.9977	0.1078
2500	0.8689	0.06211	0.9452	0.07567	0.9776	0.08666	1.0017	0.09739

[a] Compressibility factor based on a molecular weight for nitric oxide of 30.008.

Figure 13: Compressibility Factor of Nitric Oxide

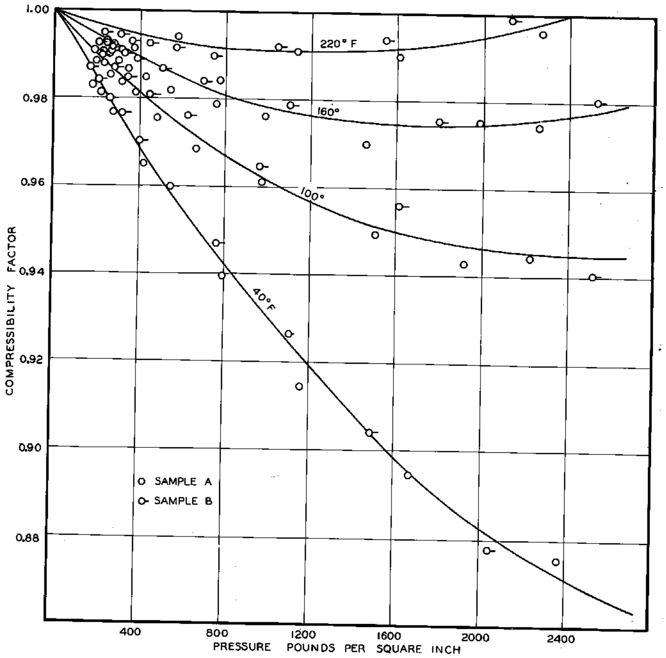
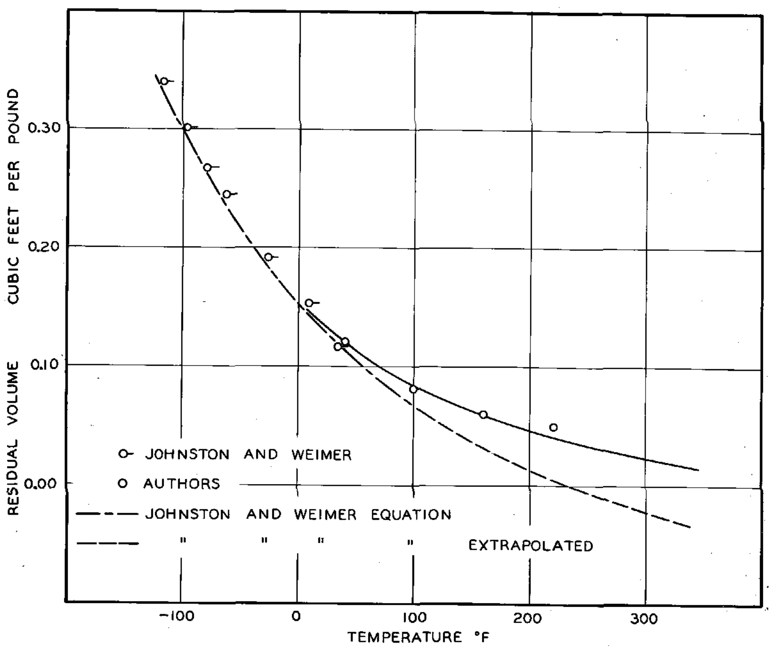


Figure 14: Residual Volume of Nitric Oxide at One Atmosphere Pressure



PART III

THE VOLUMETRIC BEHAVIOR OF SIX MIXTURES IN THE BINARY SYSTEM NITROGEN DIOXIDE - NITRIC OXIDE

INTRODUCTION TO PART III

The results of experimental measurements on nitrogen dioxide and on nitric oxide have been presented in Parts I and II, respectively, of this thesis. As discussed in the General Introduction, the primary interest of this investigation of the binary system nitrogen dioxide-nitric oxide is restricted to mixtures in which the fraction of nitric oxide present does not exceed 30 weight per cent.

The data presented in Part III are not in final form but represent only a summary of the actual experimental measurements taken until the time of writing. They represent approximately one half of those projected for the whole study. The further experiments planned will continue this investigation at lower values of specific volume and resultant higher pressures for the same ranges of temperature and composition. These future investigations await the completion of a smaller working cell, because obtaining the desired values of specific volume in the present cell would require inconveniently large amounts of material.

The initial work of importance on the gas-liquid and gas-solid equilibria in the binary system nitrogen dioxide-nitric oxide was performed by Baume and Robert (20). The results of their measurements were summarized and extended by Purcell and Cheesman (21). The measurements of the latter authors cover the temperature range from approximately -100 to 44°F and extend to a maximum value of pressure of approximately 2 atmospheres. Epstein and Cirkova (22) investigated the vapor pressures of mixtures of nitric oxide and nitrogen dioxide, the fraction of nitric oxide varying from zero to approximately 39.5 weight per cent, corresponding to the composition of the compound nitrogen trioxide (N_2O_3). The measurements of Epstein and Cirkova covered the temperature range from approximately 68 to 140°F and extended to maximum pressures of approximately 230 pounds per square inch. These authors determined the composition of each of their samples at 68°F by a combination of analytic means and a consideration ofthe published results of earlier investigators, but they did not attempt to follow the changes in the composition of the liquid phase of their samples as the temperature was increased.

APPARATUS, MATERIAL, AND METHODS

The same isochoric volumetric apparatus described in the initial section of this thesis was used to obtain the data reported in this section. The nitrogen dioxide and nitric oxide used were prepared by the techniques described in Parts I and II, respectively, and the same techniques of sample addition were used. The procedure followed was to add a sample of nitrogen dioxide to the working cell first, and then to make three consecutive additions of nitric oxide, taking an entire series of volumetric measurements after each addition of nitric oxide. The cell was cooled to 10°F during each addition of nitric oxide. This procedure was adopted to take advantage of the low vapor pressure of nitrogen dioxide as compared to that of nitric oxide. Following each set of sample additions and volumetric measurements, the cumulative sample in the cell was carefully condensed into an evacuated weighing bomb at the temperature of liquid air and weighed to provide an overall check on the amount of sample present.

A minimum of three cumulative additions of nitric oxide to each sample of nitrogen dioxide was believed to be desirable. The further systematic treatment of the single phase data involves as a first step the preparation of isothermal plots of the weight of nitric oxide added against the equilibrium pressure for each cumulative series of nitric oxide additions. The weight of nitrogen dioxide present, the total volume, and the temperature are thus held constant for each curve plotted. The three cumulative additions of nitric oxide furnish three points on such a curve, and the known properties of nitrogen dioxide furnish a fourth point. Sufficient information is then available at each temperature for a smooth curve to be drawn, from which the equilibrium pressures for even values of weight fraction of nitric oxide may be determined. This procedure places the data in a form in which they may readily be treated by the graphical procedures of cross-plotting and smoothing.

It is believed that the temperatures of measurement were known within 0.03°F relative to the international platinum scale and the pressures within 0.2 pound per square inch or 0.1 per cent, whichever is larger. The materials were introduced into the apparatus by the use of weighing bomb techniques (19) with a probable uncertainty of less than 0.1 per cent, and the total weight of sample added in each cumulative series of additions was checked to within 0.1 per cent by weighing material withdrawn at the conclusion of the series.

EXPERIMENTAL MEASUREMENTS

The volumetric behavior of six mixtures in the binary system nitrogen dioxide-nitric oxide was determined. The experimental work was divided into two portions, each consisting of three cumulative additions of nitric oxide to a fixed amount of nitrogen dioxide, the volumetric behavior of the resultant mixture being determined after each addition of nitric oxide. The measurements as a whole covered a composition range of from 5 to 20 weight per cent nitric oxide and a temperature range of from 10 to 340°F. The maximum pressure attained was approximately 600 pounds per square inch.

Figure 15 presents the results of the experimental measurements described above. The data are plotted as isochors on a pressure-temperature diagram. The two separate families of curves representing cumulative nitric oxide additions to a fixed amount of nitrogen dioxide are readily apparent, and the dew point behavior for each family of curves is indicated with a dotted line. Values of specific volume and total volume indicated in this figure are average values, because the cell undergoes small changes in total volume as the pressure and temperature are varied.

The experimental measurements plotted in Figure 15 are tabulated in Table VI. The data has, as yet, undergone no treatment other than normal calculation procedures and the application of calibration constants.

TABLE VI : Experimental Measurements on the Binary System Nitrogen Dioxide-Nitric Oxide

Group A
(weight of NO_2 = 0.089166 lb)

Wt % NO:	5.492		11.652		19.042	
V(ave) ft^3/lb:	0.3596		0.3361		0.3080	
	Temp °F	Pressure psia	Temp °F	Pressure psia	Temp °F	Pressure psia
	73.71	21.45	70.00	31.49	70.00	41.57
	100.00	39.62	100.00	56.50	100.00	76.51
	130.00	73.81	130.00	97.06	130.00	121.25
	160.00	130.05	160.00	160.36	160.00	193.16
	190.00	219.32	190.00	256.79	190.00	298.44
	200.00	257.67	200.00	298.37	200.00	342.71
	205.00	271.85	210.00	323.39	210.00	375.45
	215.00	287.08	220.00	338.45	220.00	392.97
	220.00	294.09	250.00	385.95	250.00	444.85
	250.00	339.72	280.00	434.24	280.00	497.00
	280.00	385.26	310.00	479.85	310.00	547.14
	310.00	429.58	340.00	522.10	340.00	593.76
	340.00	470.37				

TABLE VI : Continued

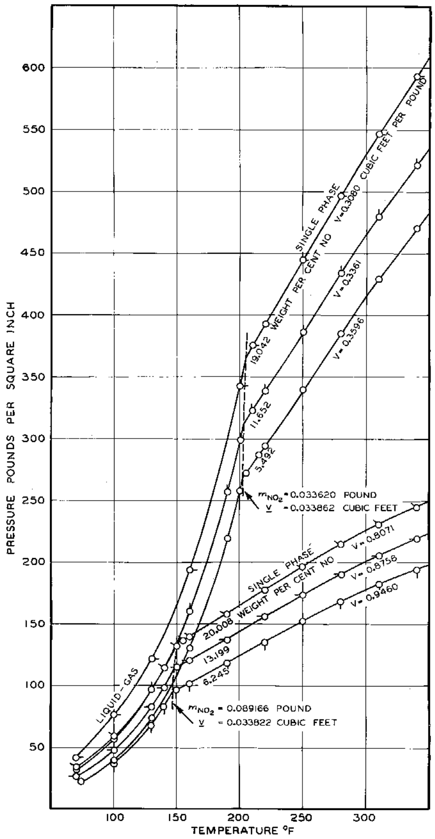
Group B
(weight of NO_2 = 0.033620 lb)

Wt % NO: 6.245 13.199 20.008

V(ave) ft^3/lb: 0.9460 0.8758 0.8071

Temp °F	Pressure psia	Temp °F	Pressure psia	Temp °F	Pressure psia
100.00	37.16	70.00	25.98	70.00	33.82
130.00	68.21	100.00	47.68	100.00	58.77
140.00	83.13	130.00	82.71	130.00	96.76
150.00	96.63	140.00	98.81	140.00	113.97
160.00	101.71	150.00	114.79	150.00	132.19
190.00	117.99	160.00	120.02	155.00	136,54
220.00	135.19	190.00	137.18	160.00	139.54
250.00	152.47	220.00	155.79	190.00	158.05
280.00	168.29	250.00	173.52	220.00	177.78
310.00	182.20	280.00	190.45	250.00	196.85
340.00	194.66	316.00	205.47	280.00	214.90
		340.00	219.50	310.00	230.61
				340.00	245.64

Figure 15: Pressure Temperature Diagram for Six Mixtures of Nitrogen Dioxide and Nitric Oxide



PART IV

THE VOLUMETRIC BEHAVIOR OF FOUR MIXTURES IN THE BINARY SYSTEM HYDROGEN SULFIDE-WATER

INTRODUCTION TO PART IV

Hydrogen sulfide is of increasing importance in petroleum production and processing operations. Moreover, in a majority of cases petroleum reservoirs involve structures whose voids are partially filled with water. Hence, there is an increasing need for accurate information about the behavior of the hydrogen sulfide-water system and eventually about the behavior of various heterogeneous hydrogen sulfide-water-hydrocarbon systems.

The Chemical Engineering Laboratory of the California Institute of Technology recently published studies of the volumetric behavior of hydrogen sulfide (23). The present work on the binary system consisting of hydrogen sulfide and water is part of an overall program which also includes studies of the binary systems formed by hydrogen sulfide and various hydrocarbons. Previous work on the hydrogen sulfide-water system by other investigators was essentially limited to investigations of the three-phase behavior. The most recent of such investigations was conducted by Scheffer (24), who also gives a critical appraisal of earlier work.

The present data represent only the initial measurements in the investigation of the binary system. These initial measurements were made in order to determine the suitability of the isochoric volumetric apparatus described in the initial section of this thesis for investigations of this binary system. It was found that the working cell underwent serious corrosion during the measurements. Accordingly, further investigations await the completion of a new working cell, the interior surface of which will be plated with either chromium or gold.

APPARATUS AND METHODS

The same isochoric apparatus and general techniques of sample addition were used as in the work described in the previous sections of this thesis. The procedure followed was to add a sample of water to the working cell first, and then to make two consecutive additions of hydrogen sulfide, taking an entire series of volumetric measurements after each addition of hydrogen sulfide. The cell was cooled to 40° F during each addition of hydrogen sulfide. This procedure was adopted in order to take advantage of the low vapor pressure of water as compared to that of hydrogen sulfide. Following each set of sample additions and volumetric measurements an attempt was made to condense the cumulative sample in the cell into an evacuated weighing bomb at the temperatures of liquid air and to weigh the amount of material withdrawn. However, it was not found possible to make a sample withdrawal in the case of one of the sets of measurements reported because of difficulties with plugged lines.

As discussed in Part III of this thesis, it would have been desirable, from a viewpoint of the later systematic treatment of the data, to make at least three cumulative additions of hydrogen sulfide to each sample of water. However, it was decided to restrict the initial work to only two additions in order to minimize the possibility of measurable changes in the composition of the sample because of reaction of the sample with the interior surface of the working cell.

It is believed that the temperatures of measurement were known within 0.03 °F relative to the international platinum scale and the pressures within 0.2 pound per square inch or 0.1 per cent, whichever is larger. The materials were introduced into the apparatus by the use of weighing bomb techniques with a probable uncertainty of less than 0.1 per cent.

MATERIAL

The water used in this study was prepared by the redistillation of material from the laboratory distilled water supply. The water was boiled at reduced pressure in order to remove traces of dissolved gases. The hydrogen sulfide was prepared by the action of distilled water on a chemically pure grade of aluminum sulfide. The gas evolved was dried over anhydrous calcium chloride and calcium sulfate and collected under vacuum at the temperature of liquid air. This technique for the preparation of hydrogen sulfide had been successfully employed in this laboratory (23). The hydrogen sulfide was stored at elevated pressures in stainless steel containers.

EXPERIMENTAL MEASUREMENTS

The volumetric behavior of four mixtures in the hydrogen sulfide-water system was determined. The experimental work was divided into two portions, each consisting of two consecutive additions of hydrogen sulfide to a fixed amount of water, the volumetric behavior of the resultant mixture being determined after each addition of hydrogen sulfide. The measurements covered a temperature range of from 10 to 340°F. The compositions used were random, and the maximum pressure attained was approximately 630 pounds per square inch.

Figure 16 presents the results of the experimental measurements described above. The data are plotted as isochors on a pressure-temperature diagram. Values of specific volume indicated in this figure are average values, because the cell undergoes small changes in total volume as the pressure and temperature are varied. It will be noted that the specific volumes of one of the sets of two mixtures reported were too small for any dew-point behavior to result at the temperatures used. Three phase behavior was encountered and is indicated with a dashed line. The present work is not particularly concerned with behavior in the three-phase region, but what information was obtained served to substantiate the findings of Scheffer (24). He found the three phases to be liquid, gas and a solid hydrate of undetermined composition. The experimental measurements plotted in Figure 16 are tabulated in Table VII.

It is believed that no appreciable error was introduced into the measurements by reaction of the samples with the interior surface of the working cell because of the constancy of measurements with time and their reproducibility upon returning to a given temperature.

TABLE VII : Experimental Measurements on the Binary System Hydrogen Sulfide-Water

A. Weight of water of 0.017073 lb.

Wt. Per Cent H_2S:	70.73		81.37	
Specific Volume : (cu.ft/lb)	0.5804		0.3695	
	Temp. °F	Pressure psia	Temp. °F	Pressure psia
	10.00	104.36	10.01	105.27
	20.00	123.55	40.00	171.36
	30.00	144.20	70.00	263.54
	40.00	151.15	80.00	298.70
	50.02	154.49	82.49	304.20
	60.00	159.10	90.00	311.96
	70.00	163.68	100.01	321.46
	71.00	163.73	130.02	348.03
	72.50	167.87	160.00	374.94
	75.00	174.94	190.02	403.19
	76.00	183.02	220.00	434.25
	77.50	183.70	250.00	469.85
	80.00	184.90	280.00	511.76
	90.00	189.60	310.01	562.18
	99.99	195.07	340.01	624.16
	130.00	209.38		
	160.01	224.48		
	189.99	241.49		
	220.00	261.45		
	250.01	285.67		
	280.00	316.45		
	310.01	356.45		
	340.00	408.16		

TABLE VII : Continued

B. Weight of water of 0.0064053 lb.

Wt. Per Cent H_2S:	42.64		66.26	
Specific Volume : (cu.ft/lb)	3.0441		1.7905	
	Temp. °F	Pressure psia	Temp. °F	Pressure psia
	40.01	22.01	10.00	47.33
	70.01	24.00	29.86	49.01
	99.99	25.66	40.00	49.70
	129.98	28.34	45.00	50.00
	160.01	32.47	47.00	50.06
	190.04	38.34	48.00	50.10
	220.00	47.57	49.00	50.17
	222.41	48.47	51.00	50.91
	250.01	61.55	51.99	51.58
	279.99	82.03	53.01	52.32
	310.00	110.36	55.00	55.64
	315.01	113.96	56.01	57.82
	330.00	117.75	58.00	59.38
	339.99	119.81	60.00	59.76
			70.01	61.28
			100.00	66.03
			160.00	76.63
			220.00	95.96
			280.00	134.55
			310.00	164.36
			312.01	164.04
			320.00	167.10
			340.00	172.36

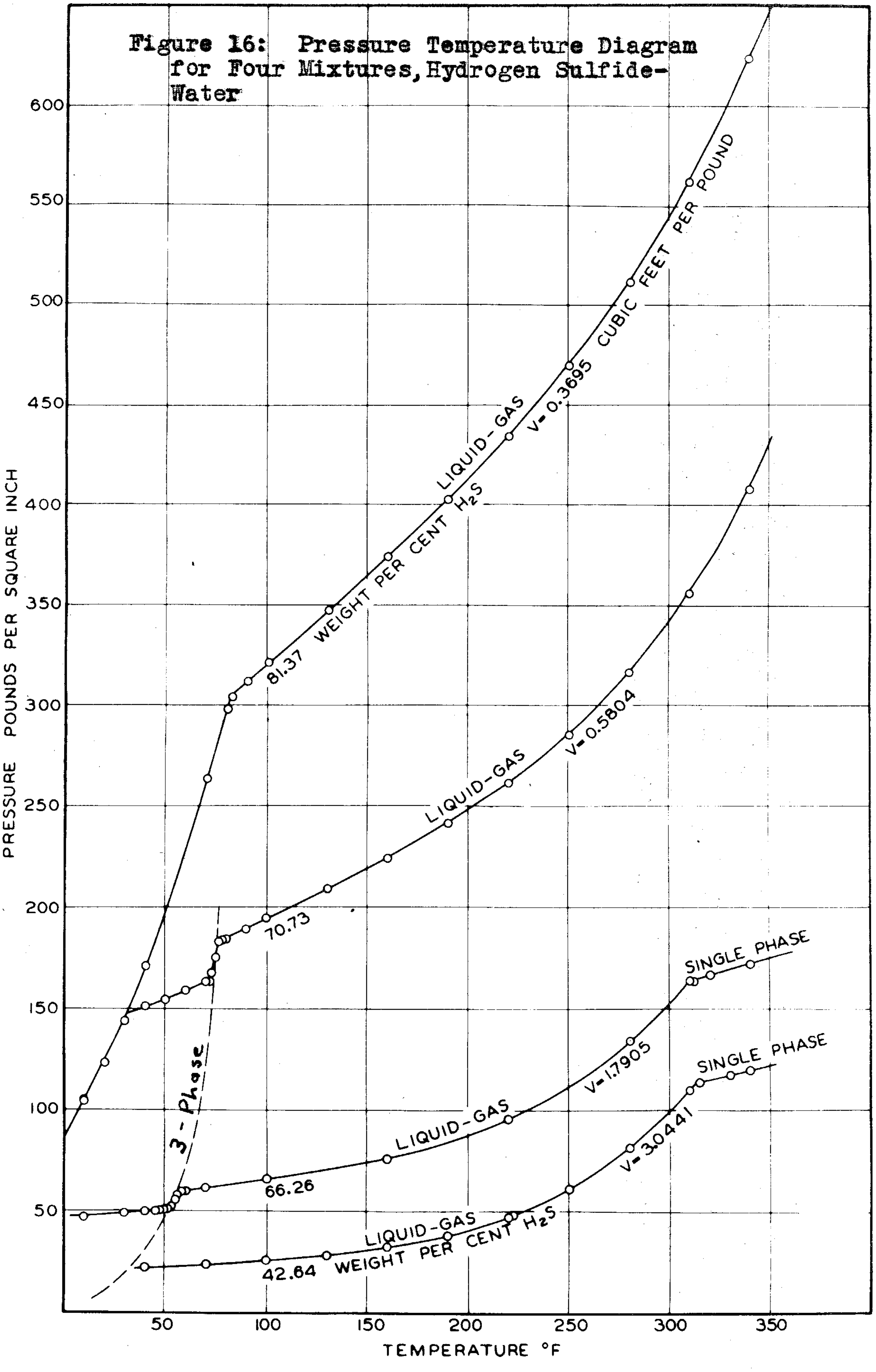


Figure 16: Pressure Temperature Diagram for Four Mixtures, Hydrogen Sulfide-Water

PART V

THERMODYNAMIC PROPERTIES OF NITRIC OXIDE

INTRODUCTION TO PART V

The engineering utility of the volumetric data upon nitric oxide presented in Part II of this thesis is enhanced by the presentation of these data in the form of thermodynamic tables. For this purpose, it is necessary to augment the volumetric data with adequate heat capacity data selected from the literature.

Heuse (25) determined heat capacities of nitric oxide calorimetrically over a limited temperature range. Heat capacities based upon equilibrium data were calculated by Shilling (26), and Partington and Shilling (27) determined the heat capacity at 7.6°C from measurements of the velocity of sound.

Several compilations exist of the properties of nitric oxide in the ideal gas state, based on statistical calculations from spectroscopic data. Johnston and Chapman (28) were the first to attack this problem successfully. Their results were, however, later revised by Witmer (29) and by Justi (30). All of these data have been analyzed and brought up to date by the American Petroleum Institute Research Project 44 (31). The properties of the oxides of nitrogen are summarized in a review article by Kobe and Pennington (32), in which these authors present an empirical equation for the standard heat capacity of nitric oxide as a function of temperature.

CALCULATIONS

The procedure followed in the calculation of entropy and of enthalpy required an initial choice at each temperature of values of enthalpy and entropy in the thermodynamic reference state, which in this case is ideal gas at a pressure of one atmosphere at each specified temperature. The isothermal changes in the values of enthalpy and entropy in going from the reference state to real conditions at each temperature, as well as values of fugacity, were then calculated as a function of pressure from the volumetric data presented in Part II of this thesis.

Values of enthalpy and entropy in the thermodynamic standard state (with a datum of ideal gas at 0°R) were taken from the tabulation of the American Petroleum Institute research project 44 (31). Interpolation of the API 44 values to the temperatures reported herein was accomplished through the use of the empirical equation of Kobe and Pennington (32) for the standard heat capacity of nitric oxide as a function of temperature. As deviations from the API 44 data of values calculated by use of this empirical equation were plotted as residuals and used to correct the interpolated values, the interpolation should involve no additional uncertainty.

Graphical techniques were used to calculate the isothermal variation in the thermodynamic properties. The fugacity was calculated from the isothermal relation:

$$\ln f_K/P = 1/b_k T \int_{P=0}^{P} \chi_k \, dP \tag{1}$$

The enthalpy was calculated from the isothermal relation:

$$H_{kP} = H_K^\circ - b_K T^2 \int_{P=0}^{P} \frac{(\partial Z_K/\partial T)_P}{P} \, dP \tag{2}$$

The entropy was calculated from the isothermal relation:

$$S_{kP} = S_K^\circ + \int_{P=0}^{1\,atm} \left(\frac{\partial \chi_K}{\partial T}\right)_P dP + b_K \int_{P=1\,atm}^{P} \frac{1-Z_K}{P} \, dP + \frac{H_{kP} - H_{k\,P=1\,atm}}{P} + b \ln \frac{1\,atm}{P} \tag{3}$$

In these equations, H_K^o and S_K° represent values of enthalpy and entropy at the thermodynamic standard state, corresponding to ideal gas at one atmosphere pressure at an assigned temperature. H_{kP} and S_{kP} represent values of enthalpy and entropy at the pressure P and the same temperature.

The residual volume, χ_K, and the compressibility factor, Z_K, indicated in the above equations are related to the prevailing pressure and specific volume by the expressions:

$$\chi_K = \frac{b_K T}{P} - V_K \tag{4}$$

$$Z_K = \frac{P V_K}{b_K T} \tag{5}$$

Table I presents the fugacity of nitric oxide, tabulated as the ratio of fugacity to pressure, f_K/P. Values of $\ln f_K/P$ are also presented. Table II presents values of the enthalpy of nitric oxide, and values of the entropy of nitric oxide are listed in Table III.

The integrations required in these thermodynamic calculations were accomplished by residual graphical operations with an uncertainty of not more than 0.1 percent. Tabulated values of fugacity should not involve uncertainties greater than 0.3 percent.

The calculation of the isothermal variation of enthalpy with pressure is dependent on accurate knowledge of the variation of compressibility factor with temperature at constant pressure. The data of Briner and coworkers (12) on the compressibility factor of nitric oxide were used to extend the volumetric data reported in this thesis to lower temperatures for the purpose of this calculation. It is believed that the uncertainties in the calculated values of the isothermal change in enthalpy as a function of pressure do not exceed a maximum of 5.0% at the extreme temperatures of 40 and 220°F and are within 2.0% in the body of the table.

The calculated values of the isothermal change in entropy with pressure are believed to involve a maximum uncertainty of 0.5%. Values of enthalpy and entropy in the thermodynamic standard state are believed to involve uncertainties of less than 0.1%.

The data are generally tabulated to more significant figures than their absolute accuracy, as indicated above, would justify. The data are tabulated in this manner, however, to preserve internal thermodynamic consistency and to assist in the computation of thermodynamic paths involving relatively small changes of state.

TABLE I : Fugacity of Nitric Oxide

Pressure, Lb./Sq.Inch Absolute	40° F		100° F	
	$-\ln f_K/P$	f_K/P	$-\ln f_K/P$	f_K/P
0	--	1.0000	--	1.0000
14.696	0.000974	0.9940	0.000707	0.9993
20	0.001327	0.9987	0.000964	0.9990
30	0.002001	0.9980	0.001450	0.9986
40	0.002681	0.9973	0.001938	0.9981
50	0.003366	0.9966	0.002427	0.9976
60	0.004058	0.9960	0.002918	0.9971
80	0.005456	0.9949	0.003902	0.9961
100	0.006874	0.9932	0.004889	0.9951
125	0.008678	0.9914	0.006124	0.9939
150	0.010513	0.9895	0.007357	0.9927
200	0.014251	0.9858	0.009815	0.9902
300	0.021901	0.9783	0.014690	0.9854
400	0.029631	0.9708	0.019447	0.9807
500	0.037321	0.9634	0.024055	0.9762
600	0.044891	0.9561	0.028516	0.9719
800	0.059591	0.9422	0.037008	0.9637
1000	0.073701	0.9290	0.044968	0.9560
1250	0.090648	0.9133	0.054220	0.9472
1500	0.106100	0.8985	0.062635	0.9393
1750	0.122746	0.8845	0.070313	0.9321
2000	0.137748	0.8715	0.077308	0.9256
2250	0.152048	0.8590	0.083700	0.9197
2500	0.165516	0.8475	0.089458	0.9144

TABLE I : Continued

Pressure, Lb./Sq. Inch Absolute	160° F		220° F	
	$-\ln f_K/P$	f_K/P	$-\ln f_K/P$	f_K/P
0	--	1.0000	--	1.0000
14.696	0.000412	0.9996	0.000243	0.9998
20	0.000560	0.9994	0.000331	0.9997
30	0.000839	0.9992	0.000496	0.9995
40	0.001118	0.9989	0.000660	0.9993
50	0.001397	0.9986	0.000825	0.9992
60	0.001675	0.9983	0.000989	0.9990
80	0.002232	0.9978	0.001317	0.9987
100	0.002787	0.9972	0.001645	0.9984
125	0.003479	0.9965	0.002051	0.9979
150	0.004170	0.9958	0.002457	0.9976
200	0.005546	0.9945	0.003258	0.9968
300	0.008274	0.9918	0.004828	0.9952
400	0.010966	0.9891	0.006330	0.9937
500	0.013610	0.9865	0.007743	0.9923
600	0.016196	0.9839	0.009053	0.9910
800	0.021168	0.9790	0.011357	0.9887
1000	0.025788	0.9745	0.013275	0.9868
1250	0.030980	0.9695	0.015275	0.9848
1500	0.035475	0.9652	0.016870	0.9833
1750	0.039345	0.9614	0.018120	0.9820
2000	0.042678	0.9582	0.019000	0.9812
2250	0.045595	0.9554	0.019488	0.9807
2500	0.048042	0.9531	0.019530	0.9807

TABLE II : Enthalpy of Nitric Oxide

Pressure Lb./Sq.Inch Absolute	Enthalpy in Btu/lb. Temperature			
	40° F	100° F	160° F	220° F
0[1]	122.750	136.950	151.090	165.470
14.696	122.605	136.812	150.978	165.379
20	122.553	136.762	150.938	165.347
30	122.454	136.668	150.864	165.285
40	122.355	136.574	150.788	165.224
50	122.256	136.481	150.714	165.162
60	122.157	136.387	150.640	165.100
80	122.960	136.200	150.490	164.977
100	121.762	136.012	150.339	164.854
125	121.515	135.778	150.154	164.699
150	121.269	135.545	149.969	164.545
200	120.775	135.077	149.605	164.238
300	119.787	134.144	148.891	163.622
400	118.800	133.215	148.200	163.008
500	117.814	132.291	147.534	162.393
600	116.827	131.372	146.886	161.781
800	114.854	129.550	145.649	160.568
1000	112.882	127.750	144.476	159.378
1250	110.417	125.535	143.086	157.937
1500	107.953	123.362	141.780	156.553
1750	105.491	121.234	140.543	155.229
2000	103.035	119.160	139.372	153.966
2250	100.605	117.137	138.252	152.755
2500	98.191	115.166	137.172	151.588

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[1] Values at zero pressure correspond to values of H°, the enthalpy at the standard state, ideal gas at one atmosphere pressure, referred to a datum of 0°R.

TABLE III : Entropy of Nitric Oxide

Entropy in Btu/lb.°R

Pressure Lb./Sq.Inch Absolute	Temperature			
	40 °F	100 °F	160 °F	220 °F
S°[1]	1.6605	1.6875	1.7117	1.7336
14.696	1.6603	1.6873	1.7115	1.7335
20	1.6403	1.6673	1.6911	1.7135
30	1.6129	1.6399	1.6641	1.6861
40	1.5936	1.6207	1.6450	1.6670
50	1.5787	1.6058	1.6301	1.6522
60	1.5665	1.5936	1.6179	1.6400
80	1.5471	1.5742	1.5987	1.6208
100	1.5321	1.5592	1.5837	1.6058
125	1.5169	1.5441	1.5686	1.5909
150	1.5045	1.5317	1.5563	1.5786
200	1.4847	1.5119	1.5368	1.5592
300	1.4564	1.4838	1.5090	1.5315
400	1.4358	1.4634	1.4890	1.5117
500	1.4196	1.4472	1.4733	1.4956
600	1.4060	1.4338	1.4603	1.4832
800	1.3840	1.4121	1.4396	1.4625
1000	1.3662	1.3946	1.4233	1.4461
1250	1.3476	1.3765	1.4066	1.4393
1500	1.3337	1.3611	1.3927	1.4270
1750	1.3176	1.3476	1.3808	1.4032
2000	1.3049	1.3355	1.3702	1.3926
2250	1.2932	1.3245	1.3608	1.3830
2500	1.2822	1.3144	1.3523	1.3744

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[1] Value of entropy at the standard state, corresponding to ideal gas at one atmosphere pressure.

PART VI

THERMODYNAMIC PROPERTIES OF NITROGEN DIOXIDE

INTRODUCTION TO PART VI

The engineering utility of the volumetric data upon nitrogen dioxide presented in Part I of this thesis is enhanced by the presentation of these data in the form of thermodynamic tables. For this purpose, it is necessary to augment to volumetric data with adequate heat capacity data selected from the literature.

The early calorimetric work on the heat capacity of nitrogen dioxide is that of Berthelot and Ogier (33), done in 1883, which covers a temperature range of 27 to 300°C. Their results indicate a negative temperature coefficient for the heat capacity, as would be expected from the fact that the heat capacity at lower temperatures also includes the heat of dissociation of nitrogen tetroxide. Giauque and Kemp (35) more recently determined values of the heat of vaporization and of the heat capacity from 15°K to the boiling point.

Kelley (34) calculated heat capacity data for the ideal gas state, using early spectral assignments. More recent heat capacity data for the ideal gas state are tabulated by Kobe and Pennington (32). These authors report that these data were furnished them by H. W. Wooley of the Bureau of Standards on the basis of newer spectroscopic data which are as yet unpublished. Kobe and Pennington also present an empirical equation for standard heat capacity as a function of temperature which satisfactorily represents those heat capacities of nitrogen dioxide which they tabulate.

CALCULATIONS

The procedure followed in the calculations of entropy and enthalpy required an initial choice at each temperature of values of enthalpy and entropy in the thermodynamic reference state, which in this case is ideal gas at a pressure of one atmosphere at a specified temperature. The isothermal changes in values of enthalpy and entropy in going from the reference state to real conditions at each temperature, as well as values of fugacity, were then calculated as a function of pressure from the volumetric data presented in Part I of this thesis.

The value of entropy of nitrogen dioxide in the thermodynamic standard state at a temperature of 77°F was taken from the latest revision of the tables of Selected Values of Chemical Thermodynamic Properties of the National Bureau of Standards (36). The datum temperature for the enthalpy of nitrogen dioxide was arbitrarily selected as 77°F, and the gas in the ideal state at this temperature was assigned an enthalpy of 200 Btu per pound.

The values of enthalpy in the ideal gas state were taken from the tabulation of Kobe and Pennington (32), as corrected to the datum temperature of 77°F. Interpolation of enthalpy values in the ideal gas state to the temperatures reported in this thesis and the calculation of the values of entropy in the thermodynamic standard state at the same temperatures were both accomplished through the use of the empirical equation of Kobe and Pennington for the standard heat capacity of nitrogen dioxide as a function of temperature. As a supplementary residual function was used to account for the deviations of this equation from the tabulated data, it is felt that no additional uncertainty is involved in the use of this equation to interpolate the values of enthalpy and compute the changes in entropy in the ideal gas state.

For the purposes of the thermodynamic calculations reported herein, the equilibrium material studied in Part I of this thesis was considered to be a pure component with a molecular weight equivalent to that of nitrogen dioxide.

Graphical techniques were used to calculate the isothermal changes in thermodynamic properties. The fugacity was calculated from the isothermal relation:

$$\ln f_K/P = 1/b_K T \int_{P=0}^{P} \underset{\sim}{V}_K \, dp \qquad (1)$$

The enthalpy was calculated independently from each of the isothermal relations:

$$H_{kP} = H^{\circ}_{kP} - b_K T^2 \int_{P=0}^{P} \frac{\left(\frac{\partial Z_k}{\partial T}\right)_P}{P} \, dP \qquad (2)$$

$$H_{kP} = H^{\circ}_{kP} - \int_{P=0}^{P} \underset{\sim}{V}_K \, dP + T \int_{P=0}^{P} \left(\frac{\partial \chi_K}{\partial T}\right)_P dP \qquad (3)$$

The calculation was made in these two independent, though equivalent, techniques in order to reduce the operator error in the calculations. The results of the two calculations were smoothed together for the final tabulation. The entropy was calculated from the isothermal relation:

$$S_K P = S_K^{\circ} + \int_{P=0}^{1\,\mathrm{atm}} \left(\frac{\partial \underset{\sim}{V}_K}{\partial T}\right)_P dP + b_K \int_{P=1\,\mathrm{atm}}^{P} \frac{(1 - Z_K)}{P} dP + \frac{H_K P - H_K P{=}1\,\mathrm{atm}}{P} + b \ln \frac{1\,\mathrm{atm}}{P} \qquad (4)$$

In these equations H_K° and S_K° represent values of enthalpy and entropy at the thermodynamic standard state, corresponding to ideal gas at one atmosphere pressure, at a specified temperature. H_{KP} and S_{KP} represent values of enthalpy and entropy at the pressure P and the same temperature.

The residual volume, $\underset{\sim}{V}_K$, and the compressibility factor, Z_K, indicated in the above equations are related to the prevailing pressure and specific volume by the expressions:

$$\underset{\sim}{V}_K = \frac{b_K T}{P} - V_K \qquad (5)$$

$$Z_K = \frac{P V_K}{b_K T} \qquad (6)$$

The integrations required in these thermodynamic calculations were accomplished by residual graphical operations with an uncertainty of not more than 0.1 percent. Tabulated values of fugacity should not involve uncertainties of greater than 0.3 percent.

The accurate calculation of the isothermal variation of enthalpy with pressure in the region of low temperatures and pressures is rendered difficult because of the large rates of change of the volumetric properties in this region. It is accordingly believed that uncertainties as large as five percent may exist in the calculation in this area. Values of the isothermal variation of enthalpy with pressure are generally felt to be within two percent, however.

The calculated values of the isothermal changes in entropy with pressure are believed to involve a maximum uncertainty of 1.0 percent. Values of enthalpy and entropy in the thermodynamic standard state are believed to involve uncertainties of less than 0.5 percent.

The data are generally tabulated to more significant figures than their absolute accuracy, as indicated above, would justify. The data are tabulated in this manner, however, to preserve internal thermodynamic consistency and to assist in the computation of thermodynamic paths involving relatively small changes of state.

Table I presents the fugacity of nitrogen dioxide, tabulated as the ratio of fugacity to pressure, f_K/P. Table II presents the calculated values of the enthalpy of nitrogen dioxide, referred to a datum of 200 Btu per pound at 77°F, and Table III lists values of the of the entropy of nitrogen dioxide. Figure 1 is a temperature-entropy diagram, including lines of constant enthalpy and constant pressure.

TABLE I: Fugacity of Nitrogen Dioxide
(Tabulated as the ratio f_K/P)

Pressure Pounds Per Sq. Inch. Absolute	Temperature 160°F f_K/P	 190°F f_K/P	 220°F f_K/P	 250°F f_K/P
0	1.0000	1.0000	1.0000	1.0000
14.696	.8394	.9116	.9567	.9785
20	.7746	.8842	.9420	.9710
30	.7075	.8389	.9157	.9570
40	.6560	.8002	.8911	.9434
50	.6150	.7663	.8682	.9323
60	.5851	.7365	.8466	.9173
80	.5286	.6844	.8082	.9048
100	.4870	..6413	.7748	.8813
125		.5966	.7381	.8540
150		.5593	.7062	.8287
200			.6935	.7824
250			.6061	.7434
300			.5667	.7076
400			.	.6454
500				.5924
Dew point Pressure:	111.24	196.35	332.83	543.93
Dew point f_K/P	.4668	.5040	.5435	.5711

Table I: Continued

Pressure Pounds per Sq. Inch Absolute		Temperature	
	280 °F	310 °F	340 °F
	f_K/P	f_K/P	f_K/P
0	1.0000	1.0000	1.0000
14.696	.9887	.9927	.9956
20	.9846	.9902	.9941
30	.9771	.9853	.9911
40	.9696	.9805	.9882
50	.9622	.9757	.9853
60	.9549	.9710	.9824
80	.9405	.9616	.9766
100	.9264	.9524	.9708
125	.9023	.9412	.9637
150	.8927	.9247	.9567
200	.8610	.9035	.9428
250	.8314	.8831	.9293
300	.8037	.8635	.9160
400	.7531	.8264	.8900
500	.7080	.7918	.8649
600	.6674	.7593	.8406
800	.5948	.6996	.7945
1000		.6452	.7511
1250		.5817	.6996
1500			.6511
1750			.6042
2000			.5569

Dew Point Pressure:	864.14	1336.5	
Dew Point f_K/P	.5730	.5599	

TABLE II: Enthalpy of Nitrogen Dioxide

(Values tabulated are in reference to a datum of 200 Btu/lb. at 77°F for ideal gas)

Pressure Pounds per Sq. Inch Absolute	Temperature 160°F H Btu/lb.	 190°F H Btu/lb.	 220°F H Btu/lb.	 250°F H Btu/lb.
0[1]	224.909	230.975	237.126	243.364
14.696	141.514	187.115	214.186	232.473
20	122.989	175.012	206.956	228.552
30	99.449	155.147	194.516	221.406
40	83.449	139.997	183.756	214.588
50	71.899	127.707	174.151	208.106
60	62.959	117.267	165.483	201.963
80	49.839	100.167	150.043	190.683
100	40.459	86.447	137.143	180.667
125		72.397	123.743	169.640
150		61.147	112.263	159.895
200			93.413	143.045
250			77.813	128.835
300			64.498	116.445
400				95.215
500				77.475
Dew Point Pressure:	111.24	196.35	332.83	543.93
Dew Point H:	36.098	45.666	56.793	70.490

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[1] Values at zero pressure correspond to values at the standard state, ideal gas at one atmosphere value.

TABLE II: Continued

Pressure Pounds per Sq. Inch Absolute	280°F H Btu/lb.	Temperature 310°F H Btu/lb.	340°F H Btu/lb.
0	249.687	256.093	262.581
14.696	244.191	253.157	260.565
20	242.245	252.105	259.846
30	238.640	250.135	258.490
40	235.103	248.183	257.145
50	231.641	246.245	255.808
60	228.251	244.325	254.480
80	221.691	240.535	251.854
100	215.417	236.809	249.270
125	207.972	232.242	246.085
150	200.967	227.784	242.958
200	188.117	219.184	236.862
250	176.597	210.989	230.948
300	166.132	203.159	225.188
400	147.532	188.489	214.028
500	131.172	174.859	203.228
600	116.342	162.079	192.658
800	89.602	135.319	171.918
1000		111.219	151.578

Dew Point Pressure:	864.14
Dew Point H:	82.226

TABLE III: Entropy of Nitrogen Dioxide

Pressure Pounds per Sq. Inch Absolute		Temperature		
	160°F S Btu/lb.°R	190°F S Btu/lb.°R	220°F S Btu/lb°R	250°F S Btu/lb.°R
S°[1]	1.2774	1.2870	1.2962	1.3052
14.696	1.1584	1.2214	1.2637	1.2888
20	1.1179	1.1911	1.2407	1.2705
30	1.0661	1.1450	1.2059	1.2433
40	1.0311	1.1113	1.1788	1.2279
50	1.0056	1.0846	1.1561	1.2037
60	.9854	1.0624	1.1336	1.1878
80	.9561	1.0268	1.1034	1.1601
100	.9228	.9988	1.0767	1.1374
125		.9707	1.0494	1.1136
150		.9483	1.0266	1.0933
200			.9899	1.0596
250			.9604	1.0322
300			.9358	1.0090
400				.9706
500				.9397
Dew Point Pressure:	111.24	196.35	332.83	543.93
Dew Point S:	.9128	.9173	.9218	.9278

---

[1] Values of entropy at the standard state, corresponding to ideal gas at a pressure of one atmosphere

TABLE III: Continued

Pressure Pounds per Sq. Inch Absolute		Temperature	
	280 °F S Btu/lb°R	310 °F S Btu/lb.°R	340 °F S Btu/lb.°R
S^o	1.3139	1.3224	1.3307
14.696	1.3069	1.3189	1.3283
20	1.2914	1.3046	1.3145
30	1.2691	1.2851	1.2951
40	1.2522	1.2698	1.2811
50	1.2383	1.2578	1.2699
60	1.2261	1.2476	1.2605
80	1.2055	1.2307	1.2451
100	1.1880	1.2167	1.2325
125	1.1684	1.2016	1.2192
150	1.1526	1.1887	1.2077
200	1.1244	1.1661	11883
250	1.1006	1.1476	1.1719
300	1.0801	1.1297	1.1574
400	1.0453	1.1038	1.1323
500	110162	1.0746	1.1114
600	.9909	1.0520	1.0905
800	.9473	1.0083	1.0546
1000		.9709	1.0219

Dew Point
Pressure: 864.14

S at Dew Point: .9356

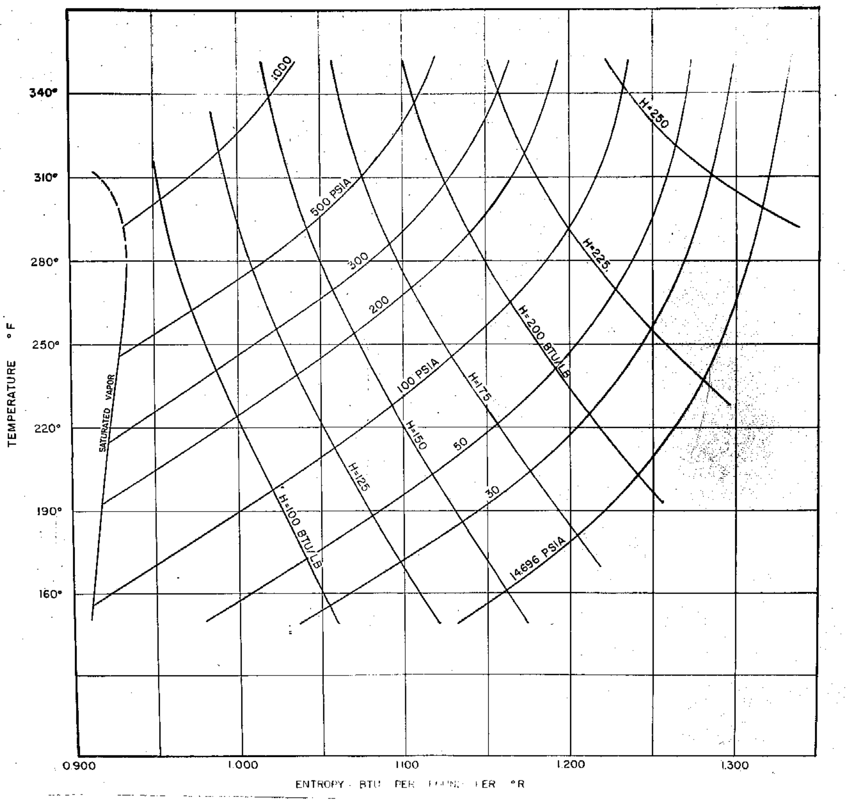

Figure 1: Temperature - Entropy Diagram for Nitrogen Dioxide[1]

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[1] All calculations based on a molecular weight of the equilibrium material taken as 46.008

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APPENDIX I

Nomenclature

b	specific gas constant, (cu.ft/lb)(lb/sq.in.)/°R
M	molecular weight
R	universal gas constant = 10.73185 (cu.ft/mole)(lb/sq.in.)/°R
P	pressure, lb/sq.in. abs
P''	two-phase pressure, lb/sq.in. abs
P_r''	reference vapor pressure, lb/sq.in. abs
$\underset{\sim}{P}''$	residual vapor pressure, lb/sq.in.
T	temperature, ° Rankine
t	temperature, ° Fahrenheit
V	specific volume, cu.ft/lb
$\underline{V}$	total volume, cu.ft
$\underset{\sim}{V}$	residual volume, cu.ft/lb
Z	compressibility factor, dimensionless